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- Vor Ablauf der für Änderungen der Ansprüche geltenden Frist; Veröffentlichung wird wiederholt, falls Änderungen eintreffen.

Zur Erklärung der Zweibuchstaben-Codes, und der anderen Abkürzungen wird auf die Erklärungen ("Guidance Notes on Codes and Abbreviations") am Anfang jeder regulären Ausgabe der PCT-Gazette verwiesen.

(54) Title: COSMETIC BASED ON OLIGOMERS AND POLYMERS CONTAINING URETHANE AND/OR UREA FUNCTIONAL GROUP

(54) Bezeichnung: KOSMETISCHES MITTEL AUF BASIS VON URETHAN- UND/ODER HARNSTOFFGRUPPEN-HALTIGEN OLIGOMEREN UND POLYMEREN

(57) Abstract: The invention relates to oligomers and polymers with urethane- and/or ureas and other functional groups, utilization of said oligomers and cosmetics which contain said oligomers and polymers.

(57) Zusammenfassung: Die vorliegende Erfindung betrifft Oligomere und Polymere mit Urethan- und/oder Harnstoffen und weiteren funktionellen Gruppen, die Verwendung dieser Oligomere und kosmetische Mittel, die diese Oligomere und Polymere enthalten.

WO 01/16200 A1

Cosmetic based on oligomers and polymers containing urethane and/or urea functional group

- 5 The present invention relates to oligomers and polymers containing urethane and/or urea groups, to the use of these oligomers in pharmaceutical and cosmetic preparations, and to cosmetic compositions comprising these oligomers and polymers.
- 10 In cosmetics, polymers with film-forming properties are used for setting, shaping and improving the structure of the hair. These hair-treatment compositions generally contain a solution of the film former in an alcohol or in a mixture of alcohol and water.
- 15 Hair-setting compositions are generally sprayed onto the hair in the form of aqueous-alcoholic solutions. Following the evaporation of the solvent, the individual hairs are held in the desired shape at their points of mutual contact by the polymer which is left behind. The polymers should on the one hand be
- 20 sufficiently hydrophilic that they can be washed out of the hair, yet on the other hand should be hydrophobic so that, even under conditions of high atmospheric humidity, the hair treated with the polymers retains its shape and the individual hairs do not stick to one another. In order to obtain a highly efficient
- 25 hair-setting effect, moreover, it is also desirable to employ polymers which have a relatively high molecular weight and a relatively high glass transition temperature (at least 10°C).

- A further demand which is currently being placed on
- 30 hair-treatment compositions is that they impart flexibility, a natural appearance and shine to the hair, for example even when the hair is naturally particularly strong and/or dark.

- When formulating hair-setting compositions, a further
- 35 consideration is that because of the environmental regulations governing the emission of volatile organic compounds (VOCs) into the atmosphere, it is necessary to reduce the content of alcohol and of propellant.
- 40 DE-A-42 25 045 and WO 94/03515 describe the use of water-soluble or water-dispersible, anionic polyurethanes as hair-setting agents. These polyurethanes are composed of

- a) at least one compound which contains two or more active
- 45 hydrogen atoms per molecule,

2

- b) at least one diol containing an acid or salt group and
- c) at least one diisocyanate.

5 The acid groups present in these polyurethanes can be converted into the corresponding salts by neutralization with at least one base. For this purpose, low molecular weight amines, such as 2-amino-2-methylpropanol, diethylaminopropylamine and triisopropanolamine, are used.

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EP-A-619 111 describes the use of polyurethanes based on organic diisocyanates, diols and 2,2-hydroxymethyl-substituted carboxylates in hair-setting compositions. At least some of the carboxylic acid groups are neutralized with an organic or
15 inorganic base, chosen from sodium hydroxide, potassium hydroxide, 2-amino-2-methylpropanol, histidine, tris(hydroxymethyl)aminomethane and triethanolamine.

DE-A-195 41 658 describes water-soluble and water-dispersible
20 graft polymers of a polyurethane prepolymer with terminal isocyanate groups and a protein containing free amino groups.

EP-A-636 361 describes a cosmetic composition which comprises, in a cosmetically compatible carrier, at least one pseudolatex based
25 on a polycondensate which contains at least one polysiloxane unit and at least one polyurethane and/or polyurea unit having anionic or cationic groups. The neutralizing agents used here are mineral bases, low molecular weight amines and aminoalcohols, mineral acids and low molecular weight carboxylic acids. WO 97/25021 has
30 a similar disclosure content. The wash-off of these film formers is unsatisfactory. In addition, because of a high siloxane content, they do not have the setting action required for a hair polymer either.

35 DE-A-195 41 329 and WO 97/17052 describe hair-treatment compositions comprising a hair-setting polymer which is dispersible or soluble in water or in a water/alcohol mixture, and additionally a water-soluble or -dispersible siloxane-containing salt. Hairspray formulations based on these
40 siloxane-containing salts, a non-siloxane-containing hair-setting polymer and a silicone oil lead to films which are readily removed from the surface of the hair, e.g. by mechanical stress. The setting action of these formulations is therefore in need of improvement.

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3

DE-A-195 41 326 and WO 97/17386 describe water-soluble or water-dispersible polyurethanes having terminal acid groups, their preparation and their use. In this case, a polyurethane prepolymer which is dispersible or soluble in water and has
5 terminal isocyanate groups is reacted with an aminosulfonic acid or aminocarboxylic acid, in particular taurine, aspartic acid and glutamic acid.

None of the abovementioned documents describes polyurethanes
10 based on diisocyanates and oligomers containing groups which are reactive toward isocyanate groups, these oligomers in turn comprising, in incorporated form, urethane and/or urea groups. The use of such oligomers in polymer-bound and non-polymer-bound form in cosmetic products is not described either.

15 Cosmetic and pharmaceutical compositions for the treatment of skin and hair are subject to special requirements with regard to their rheological properties. Thus, for example, it is a current demand that skincare products have a high proportion of care
20 substances. These are often compounds such as natural oils and fats, essential oils etc., which, because of their flow properties, can only be incorporated into the desired application form, for example stick form, using additives. Haircare products, e.g. shampoos, are also subject to specific requirements with
25 regard to their viscosity. Such products generally have a higher viscosity or a more solid consistency than is achieved with the active substances and care substances used alone. Additives for adjusting the viscosity or the consistency should preferably be used in as small amounts as possible.

30 WO-A 98/17705 describes a resin composition which comprises ester-terminated polyamides and the use thereof for the formulation of transparent gels of liquid hydrocarbons of low polarity.

35 WO-A 97/36572 describes a base composition for the preparation of cosmetic compositions which comprise at least one liquid silicone and at least one gel-forming agent. The liquid silicone is used here in amounts of from 0.5 to 95% by weight, based on the total
40 weight of the composition, the formulations illustrated by working examples comprise at least 27% by weight. The gel formers used are polymers which obligatorily comprise, in incorporated form, siloxane groups and polar groups suitable for forming hydrogen bridge bonds. The latter are chosen from ester groups,
45 urethane groups, urea groups, thiourea groups and amide groups. The polymers used as gel formers are not suitable as thickeners for oils which are not based on silicone. The thickening of oil

4

mixtures of silicone oils and further oils different therefrom is not described in this specification either.

It is an object of the present invention to provide novel
5 cosmetic compositions, in particular for the treatment of skin and hair. The cosmetic composition should preferably have good rheological properties. Cosmetic compositions in the form of hair-treatment compositions should form tack-free films with good flexible properties. These compositions should preferably impart
10 smoothness and suppleness to the hair.

Surprisingly, we have found that this object is achieved by cosmetic compositions which comprise at least one oligomer which comprises at least one diisocyanate and at least one compound
15 having at least two groups which are reactive toward isocyanate groups, where the oligomer comprises, per molecule, at least two urethane and/or urea groups and additionally at least two further functional groups having active hydrogen atoms.

20 The present invention therefore provides a cosmetic composition, comprising:

at least one oligomer or polymer of

- 25 A) at least one diisocyanate,
- B) at least one compound having at least two groups which are reactive toward isocyanate groups, which is chosen from
- 30 B1) aliphatic and cycloaliphatic polyols, polyamines and/or aminoalcohols,
- B2) polyetherols and/or diaminopolyethers,
- B3) polysiloxanes having at least two active hydrogen
35 atoms per molecule,
- B4) polyester polyols,
- and mixtures thereof, and
- 40 C) optionally at least one dicarboxylic acid and/or hydroxycarboxylic acid,

where the oligomer comprises, per molecule, at least two urethane and/or urea groups and additionally at least two
45 further functional groups chosen from hydroxyl, primary and/or secondary amino groups.

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According to a first preferred embodiment, the cosmetic compositions according to the invention comprise at least one oligomer as described above.

- 5 The cosmetic compositions according to the invention preferably comprise the oligomers in the form of a separate component and/or incorporated into a polymer. Preferred polymers which comprise the oligomers in incorporated form are polyurethanes. Within the scope of the present invention, the expression "polyurethanes"
- 10 also includes polymers which have urea groups instead of or in addition to urethane groups.

The oligomer preferably has 2 to 50, in particular 3 to 45, urethane and/or urea groups per molecule.

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Preference is given to oligomers of components A) and B) which have a molecular weight in the range from about 500 to 10 000, preferably 600 to 8 000, in particular 700 to 7 000.

- 20 Also preferred are oligomers of components A), B) and C) which have a molecular weight in the range from about 500 to 20 000, preferably 600 to 15 000, in particular 700 to 10 000.

- Oligomers which contain hydroxyl groups preferably have an
- 25 alcohol number (OH number) of from about 5 to 150 mg of KOH/g, particularly preferably 10 to 150 mg of KOH/g, in particular 20 to 100 mg of KOH/g. Oligomers which contain amino groups preferably have an amine number of from about 5 to 150 mg of KOH/g, particularly preferably 10 to 150 mg of KOH/g, especially
- 30 preferably 20 to 100 mg of KOH/g. For oligomers which have both hydroxyl and amino groups, the sum of alcohol and amine number is preferably in the range from about 5 to 150, particularly preferably 10 to 150, in particular 20 to 100.

- 35 Preferably, the oligomers do not have free isocyanate groups.

- The cosmetic compositions based on said oligomers according to the invention generally advantageously have good application properties even without the addition of components which contain
- 40 silicone groups. Thus, for example, hair-treatment compositions in which the oligomer and/or the other components of the formulation are silicone-free nevertheless generally impart good flexibility to the hair. In a preferred embodiment, the cosmetic compositions according to the invention comprise at least one
- 45 oligomer which does not include silicone groups. In a further preferred embodiment, the cosmetic compositions according to the invention comprise an oligomer which contains silicone groups,

0050/50663

6

the other components of the composition being silicone-free. In particular, both the oligomer and the other components of the cosmetic composition are silicone-free. A further suitable embodiment relates to cosmetic compositions in which the oligomer
5 and/or at least one other component contain silicone groups.

According to a second preferred embodiment, the cosmetic compositions according to the invention comprise at least one polymer of

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A) at least one diisocyanate,

B) at least one compound having at least two groups which are reactive toward isocyanate groups, which is chosen from

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B1) aliphatic and cycloaliphatic polyols, polyamines and/or aminoalcohols,

B2) polyetherols and/or diaminopolyethers,

B3) polysiloxanes with at least two active hydrogen atoms per
20 molecule,

B4) polyester polyols,

and mixtures thereof, and

25 C) optionally at least one dicarboxylic acid and/or hydroxycarboxylic acid.

The polymer preferably has 2 to 80, in particular 4 to 50, urethane and/or urea groups per molecule.

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Preference is given to polymers of components A) and B) which have a molecular weight in the range from about 700 to 40 000, preferably 1 000 to 20 000, in particular 1 500 to 15 000.

35 Preference is also given to polymers of components A), B) and C) which have a molecular weight in the range from about 700 to 80 000, preferably 1 000 to 40 000, in particular 1 500 to 20 000.

40 Polymers containing hydroxyl groups preferably have an alcohol number (OH number) of about 5 to 150 mg of KOH/g. Polymers which contain amine groups preferably have an amine number of about 5 to 150 mg of KOH/g. For polymers which have both hydroxyl and amino groups, the sum of alcohol and amine number is preferably
45 in the range from about 5 to 150.

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The polymers are preferably compatible toward hydrophobic (nonpolar) compounds, i.e. are miscible in a wide concentration range with them to form homogeneous mixtures. The polymers are particularly soluble in liquid hydrophobic compounds. Such 5 polymers are referred to below as "oil-soluble".

As well as having the urethane and/or urea groups, the polymers also preferably have further groups which are able to form hydrogen bridging bonds. These are preferably amide groups.

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Preference is given to polymers where the component B) includes at least one polyester polyol B4). In particular, component B) is chosen from polyester polyols B4) which include at least one ester of a di- or polyhydric alcohol with at least one cyclic or 15 acyclic dicarboxylic acid, obtained by dimerization of unsaturated C₆-C₃₀-carboxylic acids.

The diisocyanates A) are preferably chosen from aliphatic, cycloaliphatic and/or aromatic diisocyanates, such as 20 tetramethylene diisocyanate, hexamethylene diisocyanate, methylenediphenyl diisocyanate, 2,4- and 2,6-toluylene diisocyanate and isomeric mixtures thereof, o-, m- and p-xylylene diisocyanate, 1,5-naphthylene diisocyanate, 1,4-cyclohexylene diisocyanate, dicyclohexylmethane diisocyanate and mixtures 25 thereof, in particular isophorone diisocyanate, hexamethylene diisocyanate and/or dicyclohexylmethane diisocyanate. Particular preference is given to using hexamethylene diisocyanate. If desired, up to 3 mol% of said compounds can be replaced by triisocyanates.

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The groups of component B) which are reactive toward isocyanate groups are preferably hydroxyl groups, primary and/or secondary amino groups.

35 Preferred polyol components B1) are diols whose molecular weight is in a range from about 62 to 500 g/mol. These include, for example, diols having 2 to 18 carbon atoms, preferably 2 to 10 carbon atoms, such as 1,2-ethanediol, 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, 1,5-pentanediol, 1,10-decanediol, 40 2-methyl-1,3-propanediol, 2,2-dimethyl-1,3-propanediol, di-, tri-, tetra-, penta- and hexaethylene glycol, neopentyl glycol, cyclohexanedimethylol, glycerol monostearate and mixtures thereof.

45 Preferred components B1) are also triols and polyhydric polyols having 3 to 100, preferably 3 to 70, carbon atoms. Preferred triols are, for example, glycerol and trimethanolpropane.

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Preferred triols B1) are also the triesters of hydroxycarboxylic acids with trihydric alcohols. These are preferably triglycerides of hydroxycarboxylic acids, such as, for example, lactic acid, hydroxystearic acid and ricinoleic acid. Also suitable are
5 naturally occurring mixtures which contain hydroxycarboxylic acid triglycerides, in particular castor oil. Preferred polyhydric polyols B1) are, for example, erythritol, pentaerythritol and sorbitol.

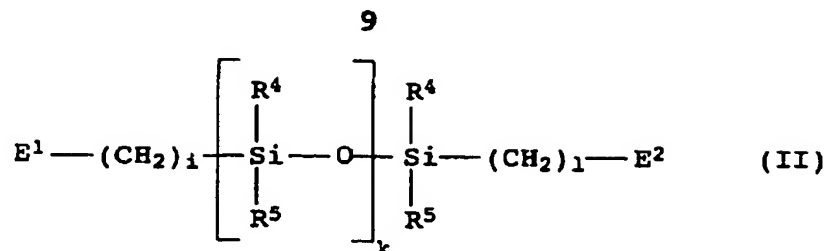
- 10 Preferred aminoalcohols B1) are, for example, 2-aminoethanol, 2-(N-methylamino)ethanol, 3-aminopropanol, 4-aminobutanol, 1-ethylaminobutan-2-ol, 2-amino-2-methyl-1-propanol, 4-methyl-4-aminopentan-2-ol etc.
- 15 Preferred polyamines B1) are, for example, diamines, such as ethylenediamine, propylenediamine, 1,4-diaminobutane, 1,5-diaminopentane and 1,6-diaminohexane. Preferred triamines B1) are, for example, diethylenetriamine, N,N'-diethyldiethylenetriamine etc. Preferred higher-valency
20 polyamines are, for example, triethylenetetramine etc.

The compounds given as component B1) can be used individually or in mixtures. Particular preference is given to using
1,2-ethanediol, 1,4-butanediol, 1,6-hexanediol, neopentyl glycol,
25 diethylene glycol, cyclohexanedimethylol and mixtures thereof.

- Component B2) is preferably a polyetherol having a number-average molecular weight in the range from about 300 to 5 000, preferably about 400 to 4 000, in particular 500 to 1500. Preferred
30 polyetherols are polyalkylene glycols, e.g. polyethylene glycols, polypropylene glycols, polytetrahydrofurans, copolymers of ethylene oxide, propylene oxide and/or butylene oxide, which contain, in copolymerized form, the alkylene oxide units in random distribution or in the form of blocks, etc.
- 35 Polytetrahydrofurans and mixtures which contain these are preferably used as component B2).

Suitable polytetrahydrofurans B2) can be prepared by cationic polymerization of tetrahydrofuran in the presence of acidic
40 catalysts, such as, for example, sulfuric acid or fluorosulfuric acid. Such preparation processes are known to the person skilled in the art.

The polysiloxanes B3) are preferably a compound of the formula II
45



in which

R^4 and R^5 independently of one another are C_1 - to C_4 -alkyl, benzyl or phenyl,

E^1 and E^2 independently of one another are OH or NHR^6 , where R^6 is hydrogen, C_1 - to C_6 -alkyl or C_5 - to C_8 -cycloalkyl,

i and l independently of one another are 2 to 8,

k is 3 to 50,

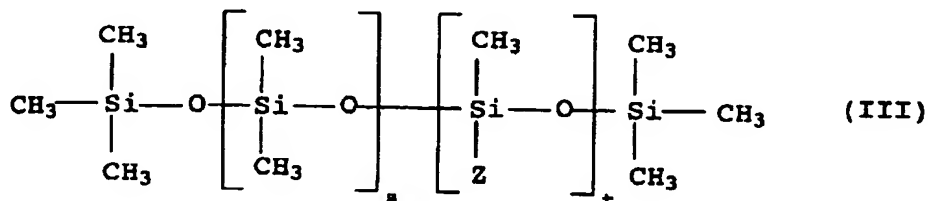
and mixtures thereof.

Suitable alkyl radicals are, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, t-butyl, n-pentyl, n-hexyl etc. Suitable cycloalkyl radicals are, for example, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl etc.

Preferably, R^4 and R^5 are both methyl.

These polysiloxanes B3) preferably have a number-average molecular weight in the range from about 300 to 5 000, preferably 400 to 3 000.

The polysiloxanes B3) are also preferably a compound of the formula III



in which

the order of the siloxane units is arbitrary,

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- s is a value from 5 to 200, preferably 10 to 100,
- t is a value from 1 to 20, preferably 2 to 10,
- 5 z is a radical of the formula $-(CH_2)_u-NH_2$, in which u is an integer from 1 to 10, preferably 2 to 6, or
- z is a radical of the formula $-(CH_2)_x-NH-(CH_2)_y-NH_2$, in which x and y independently of one another are 0 to 10, preferably
- 10 1 to 6, where the sum $x + y$ is 1 to 10, preferably 2 to 6.

These include, for example, the MAN and MAR grades from Hüls, and the Finish grades from Wacker, e.g. Finish WT 1270.

- 15 Suitable compounds B3) are also the polydimethylsiloxanes described in EP-A-227 816, to which reference is hereby made.

- Suitable polyester polyols B4) are linear and branched polymers having terminal OH groups, e.g. those having at least two OH
- 20 groups. Polyester polyols can be prepared, for example, by esterification of aliphatic, cycloaliphatic and aromatic di-, tri- and/or polycarboxylic acids, and of hydroxycarboxylic acids with di-, tri- and/or polyols. Preferred polyesterols B4) are polyesterdiols.

- 25 The polyesterols B4) preferably have a number-average molecular weight in the range from about 400 to 5 000, preferably 500 to 4 000, in particular 600 to 3 000.

- 30 Component B4) is preferably chosen from esters of di- or polyhydric alcohols with at least one carboxylic acid, the carboxylic acid being chosen from

- cyclic or acyclic dicarboxylic acids, obtained by
- 35 dimerization of unsaturated C_6 - to C_{30} -carboxylic acids,
- aliphatic, cycloaliphatic and/or aromatic C_8 - to C_{30} -dicarboxylic acids,
- aliphatic, cycloaliphatic and aromatic C_8 - to C_{30} -hydroxycarboxylic acids,

- 40 and mixtures thereof.

- The dimerization of mono- or polyunsaturated carboxylic acids gives mixtures of acyclic and cyclic dicarboxylic acids, which
- 45 are referred to as dimeric acids or dimer fatty acids. For the preparation of component B4), preference is given to using dimer fatty acid mixtures which contain dimer fatty acids having 8 to

11

54 carbon atoms. Preference is given to dimer fatty acids having, on average, 36 carbon atoms, which are obtained, for example, in the dimerization of unsaturated C₁₈-fatty acids. Dimer fatty acids are commercially available and, depending on the production, 5 contain proportions of branched mono fatty acids and trimer fatty acids. If desired, these can be separated off by distillation prior to the use of the dimer acids for the preparation of component B4). To prepare component B4), the dimer fatty acids are esterified with diols, triols and/or polyols. Preferably, for 10 the preparation of component B4), dimer fatty acids are esterified with aliphatic and/or cycloaliphatic diols, triols and/or polyols, as are described above as component B1). If desired, the alcohols can be used alone or in mixtures.

15 Preferred components B4) are also polyesterdiols, in particular those based on aromatic dicarboxylic acids, such as terephthalic acid, isophthalic acid, phthalic acid, Na or K sulfoisophthalic acid etc., aliphatic dicarboxylic acids, such as adipic acid or succinic acid etc., and cycloaliphatic dicarboxylic acids, such 20 as 1,2-, 1,3- or 1,4-cyclohexanedicarboxylic acid. Suitable diol components of these polyesterdiols B4) are, in particular, aliphatic diols, such as ethylene glycol, propylene glycol, 1,6-hexanediol, neopentyl glycol, diethylene glycol, polyethylene glycols, polypropylene glycols, 1,4-dimethylolcyclohexane.

25 Preference is given to polyesterdiols B4) based on aromatic and aliphatic dicarboxylic acids and aliphatic diols, in particular those in which the aromatic dicarboxylic acid constitutes 10 to 95 mol%, in particular 40 to 90 mol% of the total dicarboxylic 30 acid content (remainder aliphatic dicarboxylic acids).

Particularly preferred polyesterdiols B4) are the reaction products of phthalic acid/diethylene glycol, isophthalic acid/1,4-butanediol, isophthalic acid/adipic acid/1,6-hexanediol, 35 5-NaSO₃-isophthalic acid/phthalic acid/adipic acid/1,6-hexanediol, adipic acid/ethylene glycol, isophthalic acid/adipic acid/neopentyl glycol, isophthalic acid/adipic acid/neopentyl glycol/diethylene glycol/dimethylolcyclohexane and 5-NaSO₃-isophthalic acid/isophthalic acid/adipic acid/neopentyl 40 glycol/diethylene glycol/dimethylolcyclohexane, isophthalic acid/adipic acid, neopentyl glycol/dimethylolcyclohexane.

Preferred components B4) are also polyesterdiols based on linear or branched C₈- to C₃₀-di- or polycarboxylic acids. If desired, 45 these can have one or more additional functional groups, such as, for example, hydroxyl groups. Suitable di- and polycarboxylic acids are, for example, azelaic acid, dodecanedioic acid, suberic

12

acid, pimelic acid, sebacic acid, tetradecanedioic acid, citric acid, ricinoleic acid, hydroxystearic acid and mixtures thereof. Preferred diols for the preparation of this component B4) are, for example, 1,6-hexanediol, neopentyl glycol,

- 5 1,4-dimethylolcyclohexane, diethylene glycol, glycerol monostearate and mixtures thereof.

In a preferred embodiment, the cosmetic compositions according to the invention comprise at least one oligomer from component A) and B) which has at least two terminal groups having active hydrogen atoms, which are chosen from hydroxyl, primary and/or secondary amino groups.

The cosmetic compositions according to the invention preferably 15 comprise at least one oligomer which contains, in incorporated form, at least one component B4) which is chosen from esters of di- or polyhydric alcohols with at least one carboxylic acid, where the carboxylic acid is chosen from

- 20 - cyclic and acyclic dicarboxylic acids, obtained by dimerization of unsaturated C₆- to C₃₀-carboxylic acids,
 - aliphatic, cycloaliphatic and aromatic C₈- to C₃₀-dicarboxylic acids,
 - C₈- to C₃₀-hydroxycarboxylic acids
 25 and mixtures thereof.

In a preferred embodiment, the cosmetic compositions according to the invention comprise at least one oligomer from the components 30 A) and B4).

According to a further preferred embodiment, the cosmetic compositions according to the invention comprise at least one polymer of components A) and B), where component B) includes at 35 least one compound of component B4). Particular preference is given to cosmetic compositions which comprise at least one polymer of components A) and B4).

In a further preferred embodiment, the cosmetic compositions 40 according to the invention comprise at least one oligomer from component A), B) and C). The carboxylic acid C) is preferably chosen from the abovementioned cyclic and acyclic dicarboxylic acids, obtained by dimerization of unsaturated C₆- to C₃₀-carboxylic acids, aliphatic, cycloaliphatic and aromatic C₈- 45 to C₃₀-dicarboxylic acids, C₈- to C₃₀-hydroxycarboxylic acids and mixtures thereof. Component C) is particularly preferably chosen

0050/50663

13

from sebacic acid, azelaic acid, C₃₆-dimer fatty acid, ricinoleic acid, hydroxystearic acid and mixtures thereof.

The oligomers based on at least one carboxylic acid C) have 5 carboxylic ester and/or carboxamide groups, depending on the functional groups of component B).

The cosmetic compositions preferably comprise at least one oligomer from components A), B1) and C).

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Preference is given to oligomers of components A), B1) and C), which are obtainable by reacting at least one compound of the formula I

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(I)

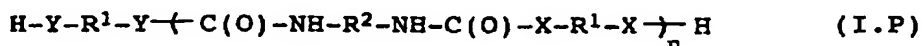
in which

- R¹ is C₂- to C₁₂-alkylene, C₅- to C₈-cycloalkylene or arylene, where alkylene radicals may be interrupted by one or two C₅- to C₈-cycloalkylene or arylene radicals,
- 20 R² is a radical derived from an aliphatic, cycloaliphatic or aromatic diisocyanate following removal of the isocyanate groups,
- A¹ is O or NR³, where R³ is hydrogen, C₁- to C₆-alkyl or C₅- to 25 C₈-cycloalkyl,

with at least one carboxylic acid C), which is chosen from cyclic or acyclic dicarboxylic acids, obtained by dimerization of unsaturated C₆- to C₃₀-carboxylic acids, aliphatic, cycloaliphatic 30 and aromatic C₈- to C₃₀-dicarboxylic acids, C₈- to C₃₀-hydroxycarboxylic acids, and mixtures thereof. In the formula I, R¹ may also be a radical derived from glycerol monostearate by removal of the OH groups.

35 The cosmetic compositions preferably comprise at least one polymer of components A), B1) and C).

Preference is given to polymers of components A), B1) and C) which are obtainable by reacting at least one compound of the 40 formula I.P



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in which

0050/50663

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- R^1 is C_2 - bis C_{12} -alkylene, C_5 - to C_8 -cycloalkylene or arylene, where alkylene radicals may be interrupted by one or two C_5 - to C_8 -cycloalkylene or arylene radicals,
- R^2 is a radical derived from an aliphatic, cycloaliphatic or aromatic diisocyanate following removal of the isocyanate groups,
- X in each repeat unit is O once and A^1 once,
- Y is O once and A^1 once,
- A^1 is O or NR^3 , where R^3 is hydrogen, C_1 - to C_6 -alkyl or C_5 - to C_8 -cycloalkyl, and
- n is an integer from 1 to 20, and preferably 1 to 5,

with at least one carboxylic C) which is chosen from cyclic or acyclic dicarboxylic acids, obtained by dimerization of unsaturated C_6 - to C_{30} -carboxylic acids, aliphatic, cycloaliphatic and aromatic C_8 - to C_{30} -dicarboxylic acids, C_8 - to C_{30} -hydroxycarboxylic acids, and mixtures thereof. In the formula I.P, R^1 may also be a radical derived from glycerol monostearate by removal of the OH groups.

- For the preparation of these oligomers of the formula I or polymers of the formula I.P, preference is given to reacting at least one diisocyanate A) of the formula $OCN-R^2-NCO$ with at least one compound B1) of the formula $HO-R^1-A^1-H$. Here, the radicals R^1 , R^2 and A^1 are as defined above.

For the preparation of the compounds of the formulae I and I.P, preference is given to using diisocyanates A) which are chosen from aliphatic diisocyanates, such as tetramethylene diisocyanate, hexamethylene diisocyanate and mixtures comprising these.

- For the preparation of the compounds of the formulae I and I.P, preference is given to using diols and aminoalcohols of the formula $HO-R^1-A^1-H$, which are chosen from the diols and aminoalcohols given above as component B1). Particular preference is given to aliphatic diols and aminoalcohols, such as 1,4-butanediol, 1,6-hexanediol, 4-aminobutanol, 6-aminohexanol and mixtures thereof.

The molar ratio of diisocyanate to compound of the formula $HO-R^1-A^1-H$ is preferably in a range from 1:1.1 to 1:2.5, preferably about 1:2.

- The oligomers of component A) and B) present in the cosmetic compositions according to the invention are prepared by reacting at least one diisocyanate A) with the groups of component B)

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which are reactive toward isocyanate groups. If, for the reaction, hydroxyl-containing components B) are used, then the reaction is generally carried out at an elevated temperature in the range from about 40 to 150°C, preferably about 70 to 120°C.

- 5 The reaction can be carried out without solvent in the melt or in a suitable solvent or solvent mixture. The suitable solvents are aprotically polar solvents, e.g. tetrahydrofuran, ethyl acetate, N-methylpyrrolidone, dimethylformamide and, preferably, ketones, such as acetone and methyl ethyl ketone. Oligomers which do not
- 10 contain hydroxyl-containing components in incorporated form are prepared by reacting the amine-containing components B) with the diisocyanates A) at a temperature in the range from about 0 to 60°C, preferably 10 to 50°C. As well as the abovementioned solvents, the preparation of oligomers which do not contain
- 15 hydroxyl-containing components in incorporated form can also be carried out in water, C₁- to C₄-alcohols, such as methanol, n-propanol, isopropanol, n-butanol and, preferably, in ethanol and ethanol/water mixtures. The reaction is preferably carried out under an inert gas atmosphere, such as, for example, under
- 20 nitrogen. Furthermore, the reaction is preferably carried out at ambient pressure or under elevated pressure. The components are preferably used in amounts such that the ratio of NCO equivalent of the compounds of component A) to equivalent of active hydrogen atom of component B) is in a range from about 0.3:1 to 1.1:1,
- 25 preferably 0.4:1 to 0.9:1.

The preparation of oligomers of components A), B) and C) is preferably carried out by reacting at least one reaction product from components A) and B) with at least one carboxylic acid C).

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- The preparation is preferably carried out without the addition of a solvent. The reaction temperature is preferably in the range from about 100 to 250°C, in particular 150 to 220°C. The water of reaction formed during the reaction is removed by customary
- 35 methods known to the person skilled in the art, such as, for example, by distillation. The reaction can be carried out at atmospheric pressure or, preferably, at reduced pressure. The polycondensation reaction can be accelerated using catalysts in the amounts customary for this purpose. Suitable catalysts are,
- 40 for example, sulfuric acid, phosphoric acid, alkyl- and arylsulfonic acids, acidic ion exchangers, tetrabutyl titanate etc.

- Oligomers of components A), B) and C) can also be prepared by
- 45 reacting at least one reaction product of components A) and B) with a derivative of an acid C). Suitable derivatives are, for

16

example, the acid halides, anhydrides and esters with C₁- to C₄-alkanols.

In the preparation of oligomers of components A), B) and C), the
5 molar ratio of reaction product from A) and B) to dicarboxylic acid or hydroxycarboxylic acid C) is preferably chosen such that the resulting oligomers essentially have no free carboxylic acid groups.

10 The polymers present in the cosmetic compositions according to the invention are generally prepared as described above for the oligomers. The reaction of components A) and B) is preferably carried out without a diluent or in the melt. The temperature is preferably in the range from about 60 to 170°C. If desired, a
15 temperature gradient can be used where, for example, the starting materials are firstly reacted for about 1 to 8 hours at a temperature in the range from about 60 to 100°C and then for about 1 to 6 hours at a temperature in the range from about 100 to 170°C. The reaction is preferably carried out under an inert gas
20 atmosphere. The resulting polymers preferably have no free isocyanate groups. Any isocyanate groups still present can be deactivated by final reaction with at least one compound having groups which are reactive toward isocyanate groups. For this purpose, preference is given to using natural or synthetic fatty
25 alcohols, fatty amines or hydroxycarboxylic acids different from C). Preference is also given to castor oil.

For the preparation of oil-soluble polymers, it is possible, preferably, to proceed according to two alternative synthesis
30 routes Syn 1 and Syn 2:

Syn 1:

- reaction of at least one dicarboxylic acid, preferably a
35 dimer fatty acid, with at least one diol to give a polyesterdiol and
- reaction of the polyesterdiol with at least one diisocyanate to give an oil-soluble polymer.

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Syn 2:

- reaction of at least one diisocyanate with at least one diol to give a urethane-containing diol or a polyurethanediol and

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0050/50663

17

- reaction of the polyurethanediol with at least one dicarboxylic acid, preferably a dimer fatty acid, to give an oil-soluble polymer.

5 Particular preference is given to synthesis route Syn 2. The reactions are preferably carried out in the melt or in an oil as solvent. Preference is given to the preparation in a cosmetically compatible oil as is also used for the formulation of cosmetic compositions which comprise the oil-soluble polymers according to
10 the invention.

The cosmetic compositions preferably comprise at least one oligomer of components A) and B1). In the preparation of these oligomers, the ratio of NCO equivalent of the compounds of
15 component A) to equivalent of active hydrogen atom of compounds of component B1) is in a range from about 0.3:1 to 0.9:1. The oligomers of components A) and B1) preferably have a molecular weight in the range from about 500 to 5 000, particularly preferably 600 to 3 000, in particular 700 to 2 000.

20 The cosmetic compositions preferably comprise at least one oligomer of components A) and B2). In the preparation of these oligomers, the ratio of NCO equivalent of the compounds of component A) to equivalent of active hydrogen atom of components
25 B2) is in a range from about 0.5:1 to 1:1, preferably 0.5:1 to 0.95:1, particularly preferably 0.5:1 to 0.8:1. The oligomers of components A) and B2) preferably have a molecular weight in a range from about 500 to 5 000, particularly preferably 600 to 3 000. Polymers of components A) and B2) preferably have a
30 molecular weight in the range up to about 15 000, particularly preferably about 6 000.

The cosmetic compositions preferably comprise at least one oligomer of components A) and B3). In the preparation of these
35 oligomers, the ratio of NCO equivalent of the compounds of component A) to equivalent of active hydrogen atom of components B3) is in a range from about 0.5:1 to 0.9:1. These polysiloxanes preferably have a number-average molecular weight in a range from about 300 to 5 000, preferably 400 to 3 000.

40 The cosmetic compositions preferably comprise at least one oligomer of components A) and B4). In the preparation of these oligomers, the ratio of NCO equivalent of compounds of component A) to equivalent of active hydrogen atom of components B4) is in
45 a range from about 0.4:1 to 1:1, preferably 0.4:1 to 0.95:1, particularly preferably 0.4:1 to 0.9:1. The molecular weight of the oligomers of components A) and B4) is preferably in a range

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from about 500 to 7 000, particularly preferably 600 to 6 000, in particular 700 to 5 000. Polymers of components A) and B4) preferably have a molecular weight in the range up to about 20 000, particularly preferably about 12 000, in particular about 5 10 000.

The cosmetic compositions preferably comprise at least one oligomer of components A), B), particularly preferably B1), and C). These reaction products preferably have a molecular weight in 10 the range from about 500 to 20 000, preferably 600 to 15 000, in particular 700 to 10 000.

The invention further provides an oligomer which comprises, in incorporated form, at least one diisocyanate A) and at least one 15 component B4), as described above.

The invention further provides an oligomer which comprises, in incorporated form, at least one diisocyanate A), at least one component B) and at least one dicarboxylic acid and/or 20 hydroxycarboxylic acid C), as described above.

In a preferred embodiment, the cosmetic compositions according to the invention comprise at least one oligomer, as described above, in the form of a separate component.

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In a preferred embodiment, the cosmetic compositions according to the invention which comprise the oligomers or the polymers as a separate component are in the form of a hair-treatment composition. These include, for example, hairsprays, setting 30 foams, hair mousse, hair gel and shampoos. Suitable components for formulating hair-treatment compositions are described in detail below for hair-treatment compositions based on polymers which comprise the oligomers in copolymerized form. Reference is made to the entire contents of the ingredients and formulations 35 cited therein. The hair-treatment compositions preferably comprise the oligomers in an amount in the range from about 0.01 to 20% by weight, preferably 0.1 to 15% by weight, based on the total amount of the composition. Generally, hair cosmetics based on the oligomers described above have better film properties, 40 such as, for example, reduced tackiness, compared with corresponding products without these additives. Better flexibility is generally achieved with the compositions according to the invention than with conventional compositions. The hair treated with the compositions according to the invention thus 45 generally has good suppleness and/or combability.

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To formulate hair-setting compositions, preference is given to using oligomers of components A) and B1).

In a further preferred embodiment, the cosmetic compositions according to the invention are in the form of an oil-containing or fat-containing cosmetic preparation. These include, for example, creams, mascara, eye makeup, face makeup, cosmetic oils, baby oil, bath oil, make-up remover, skin moisturizers, sunscreens, lipcare compositions, anhydrous hand cleansers, medicinal ointments etc.

The oil-containing or fat-containing cosmetic compositions according to the invention have, for example, an oil or fat component chosen from: hydrocarbons of low polarity, such as mineral oils; linear saturated hydrocarbons, such as tetradecane, hexadecane, octadecane etc.; cyclic hydrocarbons, such as decahydronaphthalene; branched hydrocarbons; esters, preferably esters of fatty acids, such as, for example, the esters of C_1 - to C_{24} -monoalcohols with C_1 - to C_{22} -monocarboxylic acids, such as isopropyl isostearate, n-propyl myristate, isopropyl myristate, n-propyl palmitate, isopropyl palmitate, hexacosanyl palmitate, octacosanyl palmitate, triacontanyl palmitate, dotriacontanyl palmitate, tetratriacontanyl palmitate, hexacosanyl stearate, octacosanyl stearate, triacontanyl stearate, dotriacontanyl stearate, tetratriacontanyl stearate; salicylates, such as C_1 - to C_{10} -salicylates, e.g. octyl salicylate; benzoate esters, such as C_{10} - to C_{15} -alkyl benzoates, benzyl benzoate; other cosmetic esters, such as fatty acid triglycerides, propylene glycol monolaurate, polyethylene glycol monolaurate, castor oil, C_{10} - to C_{15} -alkyl lactates, etc. The oil-containing or fat-containing cosmetic compositions according to the invention generally comprise these components in an amount of at least 0.1, preferably at least 0.2, especially at least 0.5% by weight. Suitable amounts, for example, are about 0.1 to 99.9% by weight, preferably 1 to 99.9% by weight, particularly preferably 10 to 90% by weight, especially 20 to 80% by weight, based on the total weight of the composition.

The oil-containing or fat-containing cosmetic compositions according to the invention generally comprise the oligomers and polymers described above or the reaction products thereof in an amount of from about 0.1 to 50% by weight, preferably 0.2 to 40% by weight, particularly preferably 0.2 to 30% by weight, in particular 0.5 to 10% by weight, based on the total amount of the composition.

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Furthermore, the oil-containing or fat-containing cosmetic compositions can comprise auxiliaries and/or additives, such as emulsifiers, superfatting agents, stabilizers, waxes, bodying agents, thickeners, silicone compounds, biogenic active ingredients, film formers, preservatives, hydrotropic agents, solubilizers, UV adsorbers, dyes and fragrances etc.

For the preparation of the oil- or fat-containing cosmetic compositions according to the invention, preference is given to using an oligomer which comprises, in incorporated form, at least one diisocyanate A) and at least one component B), which is chosen from components B2) to B4). For the preparation of the oil- or fat-containing compositions, preference is also given to using an oligomer of components A), B), preferably B1), and C).

The rheological properties and the consistency of the novel oil- and fat-containing cosmetic products based on oligomers described above can generally be adjusted within a wide range. Depending on the basic consistency of the cosmetic composition, it is possible to vary the properties, generally depending on the feed amount of the oligomer, from a low-viscosity to a solid consistency. Skin-cosmetic products can thus advantageously be formulated which have a high proportion of low-viscosity oil- or fat-containing components.

The oligomers described are advantageously suitable for formulating gels. The term "gel" generally means a formulation which has a higher viscosity than a liquid and is self-supporting, i.e. retains a shape given to it without a shape-stabilizing coating. To formulate gels, all of the oil components given above which are liquid at ambient temperature are generally suitable. Advantageously, gels based on the oligomers described above are generally transparent. They can be formulated with customary additives to give cosmetic compositions according to the invention, such as, for example, lipcare compositions, deodorants, antiperspirants, make-up, etc. Advantageously, the oligomers described can also be used for the preparation of gel-based non-cosmetic products. These include, for example, automotive waxes and polishes, candles, furniture polishes, leathercare compositions, metal cleaners, household cleaners, etc.

The oligomers described are also advantageously suitable for the preparation of customary O/W and W/O formulations, such as, for example, creams, in which case they may generally be used either in the oil phase or in the water phase.

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The invention further provides for the use of oligomers and reaction products thereof, as described above, as components of pharmaceutical and cosmetic preparations, preferably in cosmetic preparations for the treatment of skin or of hair, for modifying
5 rheological properties of compositions based on compounds of low polarity, and as intermediates for the preparation of water-soluble or water-dispersible polyurethanes.

The invention further provides for the use of oligomers and
10 reaction products thereof, as described above, as or in coatings and as or in treatment compositions for nonabsorbent surfaces, preferably metals, plastics, synthetic textile fibers and glass, and for absorbent surfaces, preferably wood, paper, cotton and leather.

15 Said oligomers are particularly suitable as thickeners for liquids of low polarity, preferably oils. Preference is given to using oligomers as thickeners for oils which have a proportion, based on the total weight, of urethane and/or urea groups of at
20 most 5% by weight. These components preferably have high compatibility with non-silicone-containing oils. They are generally soluble in silicone oils, non-silicone-containing oils or mixtures thereof. Advantageously, the resulting solutions are generally clear. Advantageously, clear cosmetic formulations can,
25 for example, be colored more easily than ones which are already colored. The above-described oligomers and reaction products thereof are preferably suitable for use in personal care products, such as, for example, cosmetic compositions, e.g. eye make-up, face make-up, baby oil, bath oil, make-up remover, skin
30 moisturizers, sunscreens, lipcare compositions, anhydrous hand cleansers, cosmetic gels, ointments, waxes, medicinal ointments, perfumes and suppositories. They are also advantageously suitable for formulating hair cosmetic products, such as hairsprays, setting foams, hair mousse, hair gel and shampoos. They are
35 furthermore preferably suitable for use in decorative cosmetics, in particular mascara and eyeshadows. In addition, the oligomers described above and the reaction products thereof can advantageously be used in household products, such as automotive waxes and polishes, candles, furniture polishes, metal cleaners
40 and metal polishes, household cleaners, color removers and carrier materials for insecticides. They are further suitable for use in technical or industrial products, such as, for example, in fuels, greases, soldering pastes, rust inhibitors and inkjet printer cartridges.

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The abovedescribed oil-soluble polymers are suitable, in particular, for formulating cosmetic compositions based on hydrophobic compounds.

5 The invention therefore further provides a cosmetic composition, comprising:

i) at least one oil-soluble polyurethane which comprises, in incorporated form,

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A) at least one diisocyanate,

B) at least one compound having at least two groups which are reactive toward isocyanate groups, which is chosen from

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B1) aliphatic and cycloaliphatic polyols, polyamines and/or amino alcohols,

B2) polyetherols and/or diaminopolyethers,

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B3) polysiloxanes having at least two active hydrogen atoms per molecule,

B4) polyester polyols,

and mixtures thereof, and

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C) optionally at least one dicarboxylic acid and/or hydroxycarboxylic acid,

ii) at least one cosmetically compatible hydrophobic compound,

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iii) optionally at least one cosmetic active substance different from ii) and

iv) optionally at least one additive.

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With regard to the oil-soluble polyurethanes used as component i), reference is made to the above statements regarding the polymers.

40 Component A) is preferably chosen from aliphatic diisocyanates, such as tetramethylene diisocyanate, hexamethylene diisocyanate etc. Particular preference is given to using hexamethylene diisocyanate.

45 Component B) preferably includes at least one polyester polyol B4). Component B) is preferably chosen from polyester polyols B4) which include at least one ester of a di- or polyhydric alcohol

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with at least one cyclic or acyclic dicarboxylic acid, obtained by dimerization of unsaturated C₆- to C₃₀-carboxylic acids.

The hydrophobic compounds of component ii) are chosen from
5 essentially water-insoluble (hydrophobic) cosmetically acceptable oil or fatty components. These include, preferably, water-insoluble liquids. "Water-insoluble" is understood as meaning a solubility in water of generally at most 1 g/l at 20°C. The hydrophobic compounds of component ii) are preferably chosen
10 from

I) oils, preferably mineral oils, fully synthetic oils, oils of vegetable and animal origin and essential oils, fats, saturated acyclic and cyclic hydrocarbons, esters of
15 monocarboxylic acids with mono-, di- or trihydric alcohols, silicone oils and mixtures thereof,

II) synthetic polyethylene waxes different from I),
20 III) vaseline,
and mixtures thereof.

With regard to the oil and/or fatty component I, reference is
25 made to that stated above.

The compounds of component II are preferably chosen from polyethylene waxes and wax mixtures with a proportion of incorporated ethylene units or a polyethylene proportion of at
30 least 60% by weight, based on the total weight of the compounds of component II. Examples of suitable polyethylene waxes are homopolymeric polyethylene waxes, micronized polyethylene waxes, copolymeric polyethylene waxes, oxidized polyethylene waxes, mixtures of polyethylene waxes with further waxes, such as, for
35 example, polyether waxes, montanic acid waxes, montanic ester waxes etc. The copolymeric polyethylene waxes preferably have acrylic acid or vinyl acetate as comonomers. Suitable commercially available polyethylene waxes are the Luwax® grades from BASF Aktiengesellschaft. Particular preference is given to
40 using pulverulent and granular homopolymeric polyethylene waxes (e.g. Luwax®A and AH grades), copolymeric granular polyethylene waxes (Luwax®EAS and EVA grades) and mixtures thereof.

Suitable as components (III) are natural, synthetic and slack wax
45 vaselines. These also include products with the CTFA name "Petrolatum", and the products which are primarily referred to in the USA as "petroleum jelly". Preference is given to using

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vaseline which is able to form the most uniformly coherent and resistant layer as possible. These include, preferably, grades with a low solids content and/or high viscosity. Preference is given to using the grades listed in DAB 10 (German pharmacopeia 5 10).

Preference is given to cosmetic compositions where the hydrophobic compound includes at least one component II) and/or III).

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Suitable cosmetic active substances iii) are those mentioned above. These include, preferably, vitamins, dyes, pigments, UV absorbers, care components, plant extracts, natural oils, such as olive oil, palm oil, almond oil or mixtures thereof, etc.

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Suitable additives iv) are those mentioned above. These include, in particular, emulsifiers, superfatting agents, stabilizers, waxes, bodying agents, thickeners, silicone compounds, biogenic active ingredients, film formers, preservatives, hydrotropic 20 agents, solubilizers, UV absorbers, dyes and fragrances, bactericides, perfumes, hand modifiers, etc.

The invention further provides for the use of the oil-soluble polyurethanes, as defined above, as or in cosmetic oil, pomade, 25 ointment and wax bases, and for the formulation of O/W and W/O emulsions as component of pharmaceutical and cosmetic preparations, preferably in cosmetic preparations for the treatment of the skin or of the hair, for modifying the rheological properties of compositions based on compounds of low 30 polarity, as or in coatings and as or in treatment compositions for nonabsorbent surfaces, preferably metals, plastics, synthetic textile fibers and glass, and for absorbent surfaces, preferably wood, paper, cotton and leather, and as thickeners for liquids of low polarity.

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In contrast to the polymers described, the above-described oligomers always necessarily have at least two functional groups chosen from hydroxyl and primary and secondary amino groups. They are suitable, in an advantageous manner, for constructing 40 segmented polyurethanes which have these oligomers in incorporated form as repeat unit.

The invention thus further provides segmented polyurethanes which comprise, in incorporated form, at least one oligomer, as 45 described above, at least one low molecular weight chain extender, at least one compound having at least one ionogenic

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and/or ionic (hydrophilic or dispersion-active) group and at least one diisocyanate.

The polyurethanes based on the oligomers described above are
5 water-soluble or water-dispersible.

The oligomers described above are particularly suitable as components for the preparation of water-soluble or water-dispersible polyurethanes. The invention further provides
10 water-soluble or water-dispersible polyurethanes of:

- a) at least one oligomer, as described above,
- b) at least one compound having a molecular weight in the range from 56 to 600, which contains two active hydrogen atoms per
15 molecule,
- c) at least one compound which has two active hydrogen atoms and at least one ionogenic and/or ionic group per molecule,
- d) optionally at least one polymer having at least two active hydrogen atoms per molecule,
- 20 e) at least one diisocyanate.

The polyurethanes according to the invention comprise at least one of the oligomers described above as component a) in incorporated (copolymerized) form.

25 Component b) is preferably a diol, diamine, amino alcohol, or a mixture thereof. The molecular weight of these compounds is preferably in a range from about 56 to 500. If desired, up to 3 mol% of said compounds can be replaced by triols or triamines.

30 Preference is given to using diols as component b). Diols which can be used are, for example, ethylene glycol, propylene glycol, butylene glycol, neopentyl glycol, cyclohexanedimethylol, di-, tri-, tetra-, penta- or hexaethylene glycol and mixtures thereof.
35 Preference is given to using neopentyl glycol, glycerol monostearate and/or cyclohexanedimethylol.

Suitable aminoalcohols b) are, for example, 2-aminoethanol, 2-(N-methylamino)ethanol, 3-aminopropanol, 4-aminobutanol,
40 1-ethylaminobutan-2-ol, 2-amino-2-methyl-1-propanol, 4-methyl-4-aminopentan-2-ol etc.

Suitable diamines b) are, for example, ethylenediamine, propylenediamine, 1,4-diaminobutane, 1,5-diaminopentane and
45 1,6-diaminohexane.

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Suitable diamines b) are also diamines of the formula $R^a-NH-(CH_2)_{2-3}-NH_2$, where R^a is C_8- to C_{22} -alkyl or C_8- to C_{22} -alkenyl, where the alkylene radical can have 1, 2 or 3 nonadjacent double bonds. The molecular weight of these diamines 5 b) is preferably in a range from about 160 to 400.

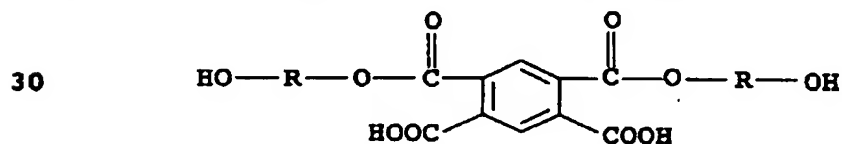
Other suitable diamines b), which are customarily used as chain extenders, are, for example, hexamethylenediamine, piperazine, 1,2-diaminocyclohexane, 1,3-diaminocyclohexane, 10 1,4-diaminocyclohexane, neopentanediamine, 4,4'-diaminodicyclohexylmethane etc.

Suitable compounds c) have two active hydrogen atoms and at least one ionogenic and/or ionic group per molecule, the groups being 15 anionogenic, anionic, cationogenic or cationic.

Preferred compounds c) having two active hydrogen atoms and at least one anionogenic and/or anionic group per molecule are, for example, compounds containing carboxylate and/or sulfonate 20 groups. Particularly preferred components c) are 2,2-hydroxymethylalkylcarboxylic acids, such as dimethylolpropanoic acid, and mixtures which contain 2,2-hydroxymethylalkylcarboxylic acids, such as dimethylolpropanoic acid.

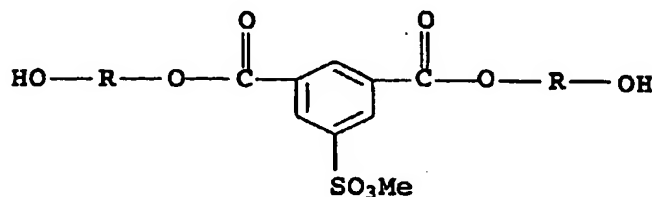
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Suitable diamines and/or diols c) having anionogenic or anionic groups are compounds of the formula



and/or

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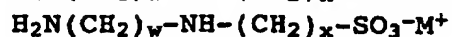
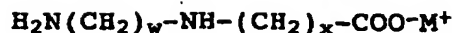


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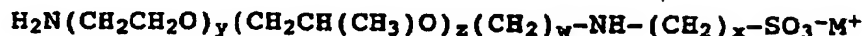
in which R is in each case a C_2-C_{18} -alkylene group, and Me is Na or K.

45 As component c) it is also possible to use compounds of the formula

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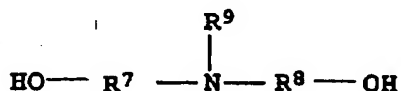
in which w and x independently of one another are an integer from 5 1 to 8, in particular from 1 to 6, and M is Li, Na or K, and compounds of the formula



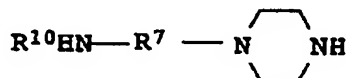
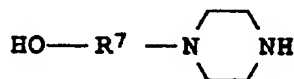
- 10 in which w and x are as defined above, y and z independently of one another are an integer from 0 to 50, where at least one of the two variables y or z is > 0. The order of the alkylene oxide units is arbitrary. The last-named compounds preferably have a number-average molecular weight in the range from about 400 to 3 000. A suitable compound of this type is, for example Poly ESP 520 from Raschig.

The polyurethanes can also comprise, in incorporated form, compounds c) which have two active hydrogen atoms and at least one cationogenic and/or cationic group, preferably at least one nitrogen-containing group, per molecule. The nitrogen-containing group is preferably a tertiary amino group or a quaternary ammonium group. Preference is given, for example, to compounds of the formulae

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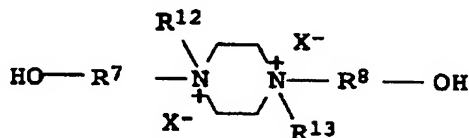
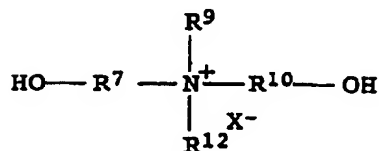
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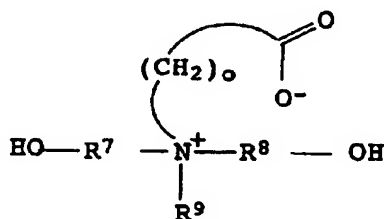
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in which

- R⁷ and R⁸, which can be identical or different, are C₂-C₈-alkylene,
- 5 - R⁹, R¹² and R¹³, which can be identical or different, are C₁-C₆-alkyl, phenyl or phenyl-C₁-C₄-alkyl,
- R¹⁰ and R¹¹, which can be identical or different, are H or C₁-C₆-alkyl,
- o is 1, 2 or 3,
- 10 X[⊖] is chloride, bromide, iodide, C₁-C₆-alkyl sulfate or SO₄²⁻/2.

Particular preference is given to N-(C₁-C₆-alkyl)diethanolamines, such as methyldiethanolamine and N-alkyl-dialkylene-triamines such
15 as N-methyl-dipropylenetriamine. These are preferably used in combination with dimethylolpropanoic acid as component c).

Also suitable as component c) are mixtures comprising two or more of the abovementioned compounds having anionic and/or anionogenic
20 groups, two or more of the abovementioned compounds having cationic and/or cationogenic groups or mixtures which comprise at least one of the abovementioned compounds having anionic or anionogenic groups and at least one of the abovementioned
compounds having cationic or cationogenic groups. Preference is
25 given to using, for example, mixtures which comprise dimethylolpropanoic acid and N-methyldiethanolamine. In a preferred embodiment, the polyurethanes comprise predominantly or exclusively anionogenic and/or anionic groups as ionogenic and/or ionic groups. In a further preferred embodiment, the
30 polyurethanes comprise predominantly or exclusively cationogenic and/or cationic groups as ionogenic and/or ionic groups. The polyurethanes thus preferably comprise a component c) in incorporated form which comprises predominantly, preferably in an amount of at least 80% by weight, in particular in an amount of
35 at least 90% by weight, based on the total amount of component c), either anionogenic (anionic) compounds or cationogenic (cationic) compounds.

Component d) is preferably a polymer having a number-average
40 molecular weight in the range from about 300 to 5 000, preferably from about 400 to 4 000, in particular from 500 to 3 000. Polymers d) which may be used are, for example, polyesterdiols, polyetherols, polysiloxanes and mixtures thereof. Polyetherols are preferably polyalkylene glycols, for example polyethylene
45 glycols, polypropylene glycols, polytetrahydrofurans etc., copolymers of ethylene oxide and propylene oxide or block copolymers of ethylene oxide, propylene oxide and butylene oxide

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which contain, in copolymerized form, the alkylene oxide units in random distribution or in the form of blocks. α,ω -Diamino-polyethers which can be prepared by amination of polyalkylene oxides with ammonia are also suitable. Preference is given to using polyesterdiols or mixtures which contain them as component d).

Suitable polytetrahydrofurans d) can be prepared by cationic polymerization of tetrahydrofuran in the presence of acidic catalysts, such as, for example, sulfuric acid or fluorosulfuric acid. Such preparation processes are known to the person skilled in the art.

Preferred polyesterdiols d) have a number-average molecular weight in the range from about 400 to 5 000, preferably from 500 to 3 000, in particular, from 600 to 2 000.

Suitable polyesterdiols are all those which are normally employed to prepare polyurethanes, especially those based on aromatic dicarboxylic acids, such as terephthalic acid, isophthalic acid, phthalic acid, Na- or K-sulfoisophthalic acid, etc., on aliphatic dicarboxylic acids, such as adipic or succinic acid, etc., and on cycloaliphatic dicarboxylic acids, such as 1,2-, 1,3- or 1,4-cyclohexanedicarboxylic acid. Particularly suitable diols are aliphatic diols, such as ethylene glycol, propylene glycol, 1,6-hexanediol, neopentyl glycol, diethylene glycol, polyethylene glycols, polypropylene glycols, 1,4-dimethylolcyclohexane.

Preference is given to polyesterdiols based on aromatic and aliphatic dicarboxylic acids and aliphatic diols, especially those in which the aromatic dicarboxylic acid accounts for from 10 to 95 mol%, in particular from 40 to 90 mol% of the overall dicarboxylic acid content (the remainder being aliphatic dicarboxylic acids).

Particularly preferred polyesterdiols are the reaction products of phthalic acid/diethylene glycol, isophthalic acid/1,4-butanediol, isophthalic acid/adipic acid/1,6-hexanediol, 5-NaSO₃-isophthalic acid/phthalic acid/adipic acid/1,6-hexanediol, adipic acid/ethylene glycol, isophthalic acid/adipic acid/neopentyl glycol, isophthalic acid/adipic acid/neopentyl glycol/diethylene glycol/dimethylolcyclohexane, and 5-NaSO₃-isophthalic acid/isophthalic acid/adipic acid/neopentyl glycol/diethylene glycol/dimethylolcyclohexane, isophthalic acid/adipic acid, neopentylglycol/dimethylolcyclohexane.

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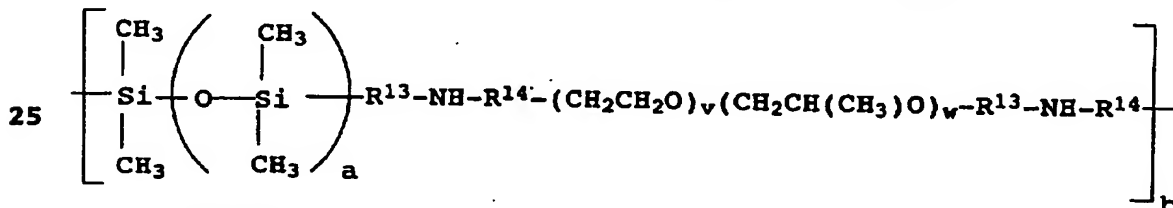
Also preferred as component d) are the polyesterdiols already given above as component B4) which are based on linear or branched, C₈- to C₃₀-di- or polycarboxylic acids and C₈- to C₃₀-hydroxycarboxylic acids. Preferred carboxylic acids and hydroxycarboxylic acids are, for example, azelaic acid, dodecanedioic acid, subaric acid, pimelic acid, sebacic acid, tetradecanedioic acid, citric acid, ricinoleic acid, hydroxystearic acid and mixtures thereof. The diol component used for the preparation of these polyesterdiols is preferably 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, neopentyl glycol, 1,4-dimethylolcyclohexane, diethylene glycol, glycerol monostearate and mixtures thereof.

Also preferred as component d) are the abovementioned polysiloxanes B3). Preferably, only one of the components a) or d) comprises a polysiloxane.

Component d) is also preferably a diaminopolyether siloxane of the formula IV which is chosen from

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- polysiloxanes having repeat units of the formula IV.1



in which

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a is an integer from 0 to 100,

b is an integer from 1 to 8,

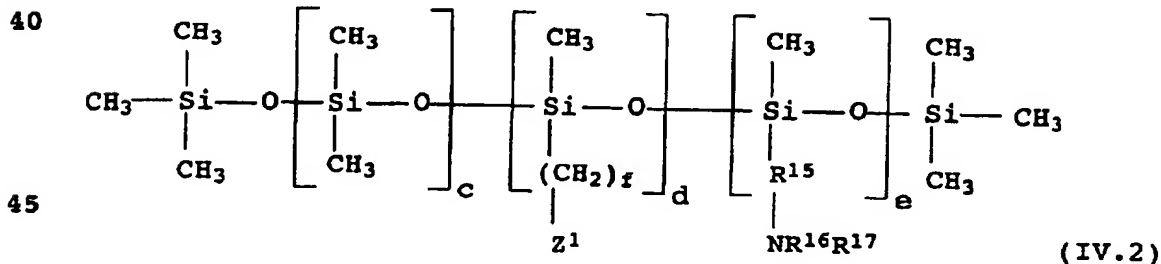
R¹³ and R¹⁴ independently of one another are C₁- to C₈-alkylene,

the order of the alkylene oxide units is arbitrary and v and w independently of one another are an integer from 0 to 200, where the sum v + w is > 0,

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- polysiloxanes of the formula IV.2

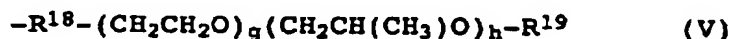
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in which

- R^{15} is a C_1 - to C_8 -alkylene radical,
 R^{16} and R^{17} independently of one another are hydrogen, C_1 - to
5 C_8 -alkyl or C_5 - to C_8 -cycloalkyl,
the order of the siloxane units is arbitrary, c, d and e
independently of one another are 0 to 100, where the sum
c + d + e is at least 3,
f is an integer from 2 to 8,
10 Z^1 is a radical of the formula V



in which

- 15 the order of the alkylene oxide units is arbitrary and g
and h independently of one another are an integer
from 0 to 200, where the sum g + h is > 0,
 R^{18} is a C_1 - to C_8 -alkylene radical, and
20 R^{19} is hydrogen or a C_1 - to C_8 -alkyl radical,

and mixtures thereof.

- Preferably, in formula IV.1, R^{13} and R^{14} independently of one
another are a C_2 - to C_4 -alkylene radical. In particular, R^{13} and
25 R^{14} independently of one another are a C_2 - to C_3 -alkylene radical.

The molecular weight of the compound of the formula IV.1 is
preferably in a range from about 300 to 100 000.

- 30 In the formula IV.1, a is preferably an integer from 1 to 20,
such as, for example, from 2 to 10.

- The total number of alkylene oxide units in the compound of the
formula IV.1, i.e. the sum v + w, is preferably in a range from
35 about 3 to 200, preferably from 5 to 180.

- Preference is given to the end groups of the polysiloxanes having
repeat units of the formula IV.1 selected from $(CH_3)_3SiO$, H,
40 C_1 - C_8 -alkyl and mixtures thereof.

- Suitable alkoxyated siloxaneamines of the formula IV.1 are
described, for example, in WO-A-97/32917, to the entire contents
of which reference is made here. Commercially available compounds
are, for example, the Silsoft® products from Witco, e.g. Silsoft®
45 A-843.

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Preferably, in the formula IV.2, the radical R¹⁵ is a C₂-C₄-alkylene radical.

Preferably, in the formula IV.2, R¹⁶ and R¹⁷ independently of one another are hydrogen or C₁-C₄-alkyl.

Preferably, the sum c + d + e is chosen such that the molecular weight of the compound of the formula IV.2 is in a range from about 300 to 100 000, preferably from 500 to 50 000.

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Preferably, the total amount of alkylene oxide units in the radical of the formula V, i.e. the sum g + h, is in a range from about 3 to 200, preferably from 5 to 80.

15 Preferably, in the formula V, the radical R¹⁸ is C₂-C₄-alkyl.

Preferably, in the formula V, the radical R¹⁹ is hydrogen or C₁-C₄-alkyl.

20 A suitable compound of the formula IV.2 is, for example, Silsoft® A-858 from Witco.

Component e) is a customary aliphatic, cycloaliphatic and/or aromatic diisocyanate, such as tetramethylene diisocyanate, 25 hexamethylene diisocyanate, methylenediphenyl diisocyanate, 2,4- and 2,6-tolylene diisocyanate and isomer mixtures thereof, o-, m- and p-xylylene diisocyanate, 1,5-naphthylene diisocyanate, 1,4-cyclohexylene diisocyanate, dicyclohexylmethane diisocyanate and mixtures thereof, especially isophorone diisocyanate, 30 hexamethylene diisocyanate and/or dicyclohexylmethane diisocyanate. If desired, up to 3 mol% of said compounds can be replaced by triisocyanates.

The polyurethanes according to the invention are prepared by 35 reacting at least one oligomer a) and the compounds of components b) and c), and optionally d), with the diisocyanate component e). Here, the ratio of NCO equivalent of component e) to equivalent of active hydrogen atom of components a) to d) is generally in a range from about 0.6:1 to 1.4:1, preferably 0.8:1 to 1.2:1, in 40 particular 0.9:1 to 1.1:1. The reaction can preferably be carried out without solvents or in a suitable inert solvent or solvent mixture. Suitable solvents are aprotically polar solvents, e.g. tetrahydrofuran, ethyl acetate, N-methylpyrrolidone, dimethylformamide and, preferably, ketones, such as acetone and 45 methyl ethyl ketone. The reaction is preferably carried out under an inert gas atmosphere, such as, for example, under nitrogen. In addition, the reaction is preferably carried out at ambient

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pressure or under increased pressure. If components a) to d) contain hydroxyl-containing compounds, then the reaction temperature is preferably in a range from about 50 to 150°C. The reaction is then preferably carried out in a solvent or solvent mixture which does not have active hydrogen atoms. Preference is given to using ketones, such as acetone, methyl ethyl ketone and mixtures thereof. If, as components a) to d), compounds which have primary and/or secondary amino groups as the groups reactive toward isocyanate groups are used exclusively or predominantly, then the reaction temperature is preferably in a range from about 5 to 80°C, particularly preferably 5 to 40°C. The reaction can then, if desired, be carried out in a solvent or solvent mixture which may have active hydrogen atoms. In addition to those given above, preference is then given to using alcohols, such as methanol and ethanol, mixtures of alcohols and water, and mixtures of alcohols and the abovementioned ketones. If the resulting polyurethanes still have free isocyanate groups, then these are then deactivated by adding amines, preferably aminoalcohols. Suitable aminoalcohols are those given above, preferably 2-amino-2-methyl-1-propanol.

The oligomers a) used for the preparation of the polyurethanes according to the invention can, in accordance with a suitable embodiment, as already described, be prepared separately and be isolated and/or purified by customary methods prior to use in the polyurethane preparation.

According to a preferred embodiment, the preparation of the oligomers a) and the preparation of the polyurethanes according to the invention is carried out without isolation of an intermediate. The two reactions preferably take place one after the other in the same reaction vessel.

The polyurethanes preferably comprise

- 35 - 0.3 to 50% by weight, preferably 0.5 to 40% by weight, of at least one oligomer a),
- 0.5 to 25% by weight, preferably 1 to 20% by weight, of at least one component b),
- 40 - 0.5 to 50% by weight, preferably 3 to 45% by weight, of at least one component c),
- 45 - 0 to 25% by weight, preferably 0.01 to 15% by weight, of at least one component d),

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- 25 to 60% by weight, preferably 35 to 53% by weight, of at least one component e)

in copolymerized form.

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The polyurethanes which contain acid groups can be partially or completely neutralized with a base. The polyurethanes which contain amine groups can be partially or completely protonated or quaternized.

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The resulting salts of the polyurethanes generally have better water solubility or dispersibility in water than the non-neutralized polyurethanes. Bases which can be used to neutralize the polyurethanes are alkali metal bases, such as sodium

- 15 hydroxide solution, potassium hydroxide solution, sodium carbonate, sodium hydrogencarbonate, potassium carbonate or potassium hydrogencarbonate, and alkaline earth metal bases, such as calcium hydroxide, calcium oxide, magnesium hydroxide or magnesium carbonate, and ammonia and amines. Suitable amines are, 20 for example, C₁-C₆-alkylamines, preferably n-propylamine and n-butylamine, dialkylamines, preferably diethylpropylamine and dipropylmethylamine, trialkylamines, preferably triethylamine and triisopropylamine, C₁-C₆-alkyldiethanolamines, preferably methyl- or ethyldiethanolamine and di-C₁-C₆-alkylethanolamines, and 25 glucamine and methylglucamine. 2-Amino-2-methyl-1-propanol, diethylaminopropylamine and triisopropanolamine have proven successful for the neutralization of polyurethanes which contain acid groups, particularly for use in hair-treatment compositions. Polyurethanes which contain acid groups can also be neutralized 30 using mixtures of two or more bases, e.g. mixtures of sodium hydroxide solution and triisopropanolamine. Depending on the intended use, the neutralization can be partial, e.g. up to 20 to 40%, or complete, i.e. up to 100%.

- 35 Because of their cationic groups, polyurethanes which contain amine groups or protonated or quaternized amine groups are generally readily soluble in water or water/alcohol mixtures or are at least dispersible without the aid of emulsifiers. Charged cationic groups can be produced from the tertiary amine nitrogens 40 present either by protonation, e.g. with carboxylic acids, such as lactic acid, or mineral acids, such as phosphoric acid, sulfuric acid and hydrochloric acid, or by quaternization, e.g. with alkylating agents, such as C₁- to C₄-alkyl halides or sulfates. Examples of such alkylating agents are ethyl chloride, 45 ethyl bromide, methyl chloride, methyl bromide, dimethyl sulfate and diethyl sulfate.

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Polyurethanes which have both cationogenic and also anionogenic groups can be subjected successively to neutralization with at least one acid, neutralization with at least one base and, if desired, additionally to quaternization. The order of the 5 neutralization steps is generally arbitrary.

If, in the preparation of the polymeric salts, a water-miscible organic solvent is used, then this can be removed immediately afterwards by customary processes known to the person skilled in 10 the art, e.g. by distillation at reduced pressure. Prior to removal of the solvent, water can additionally be added to the polymeric salt. Replacement of the solvent by water gives a solution or dispersion of the polymeric salt, from which, if desired, the polymeric salt can be obtained in the usual manner, 15 e.g. by spray drying.

The pH of the aqueous solutions or dispersions can be adjusted by adding an acid or base. Suitable acids and bases are those given above as additional neutralizing agents. The pH for anionic 20 polymeric salts is preferably in the alkaline range, in particular > 7.5 . Preferably, the pH for cationic polyurethanes is in the acidic range, in particular from 5.5 to 6.5.

The polyurethanes according to the invention are soluble in water 25 or dispersible in water. They generally form clear and tack-free films and can be washed out very readily with water. Advantageously, the polyurethanes according to the invention also give films having a very good elasticity. This elasticity is generally higher than the elasticity which is usually obtained in 30 the case of polyurethanes known from the prior art. Hair-treatment compositions based on these polymers impart very good suppleness to the hair.

The polyurethanes or polyureas according to the invention are 35 generally soluble or dispersible in alcohols, alcohol/water mixtures and/or in water without the aid of emulsifiers. Preferred alcohols for the preparation of formulations of the polyurethanes according to the invention are, in particular, C_1 - to C_4 -alkanols, such as methanol, ethanol, n-propanol, 40 isopropanol, n-butanol and mixtures thereof.

The polyurethanes according to the invention can be used as auxiliaries in cosmetics, preferably as or in coatings for keratin-containing and keratin-analogous surfaces, such as hair, 45 skin and nails. They are particularly suitable for hair cosmetics, preferably as setting polymers in hairsprays, setting foams, hair mousse, hair gel and shampoos. They are also

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preferably suitable for use in decorative cosmetics, in particular in mascara, make-up and eyeshadows. They can also be advantageously used as polymeric emulsifiers or co-emulsifiers for the formulation of cosmetic or pharmaceutical preparations 5 for the skin. Because of their hydrophilic and hydrophobic properties, they are suitable both for oil- and fat-containing preparations, and for O/W and W/O emulsions. The polyurethanes according to the invention can also be used as auxiliaries in pharmacy, preferably as or in coatings or binders for solid 10 medicament forms. The polyurethanes mentioned above can also be used in creams and as tablet coatings and tablet binders. They are also suitable as binders and adhesives for cosmetic products. The polyurethanes according to the invention are also preferably suitable for use as or in coatings for the textile, paper, 15 printing, leather and adhesives industry.

The invention also provides a cosmetic or pharmaceutical composition which comprises at least one polyurethane according to the invention. The composition generally comprises the 20 polymeric salts in an amount in the range from about 0.2 to 30% by weight, preferably from 0.5 to 20% by weight, based on the total weight of the composition.

The cosmetic compositions according to the invention are suitable 25 in particular as coating compositions for keratin-containing and keratin-analogous surfaces (hair, skin and nails). The compounds used therein are water-soluble or water-dispersible. If the compounds used in the compositions according to the invention are water-dispersible, they can be used in the form of aqueous 30 microdispersions having particle diameters of customarily from 1 to 350 nm, preferably from 1 to 250 nm. The solid contents of the preparations is usually in a range from about 0.5 to 20% by weight, preferably from 1 to 12% by weight. These microdispersions do not generally require emulsifiers or 35 surfactants for their stabilization.

Preferably, the compositions according to the invention can be in the form of a hair-treatment composition, such as setting foam, hair mousse, hair gel, shampoo and, in particular, in the form of 40 a hairspray. For use as hair-setting compositions, preference is here given to compositions which comprise polyurethanes which have at least one glass transition temperature T_g of $\geq 10^\circ\text{C}$, preferably $\geq 20^\circ\text{C}$. The K value of these polymers (measured in accordance with E. Fikentscher, Cellulose-Chemie 13 (1932), pp. 45 58-64) on a 1% strength by weight solution in N-methylpyrrolidone, is preferably in a range from 23 to 90, in particular from 25 to 60. If the polyurethanes according to the

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invention have siloxane groups, then the siloxane content of these polymers is generally from 0.05 to 20% by weight, based on the total weight of the incorporated components.

- 5 The compositions are preferably hair-treatment compositions. They are usually in the form of an aqueous dispersion or in the form of an alcoholic or aqueous-alcoholic solution. Examples of suitable alcohols are ethanol, propanol, isopropanol etc.
- 10 In addition, the hair-treatment compositions according to the invention can generally comprise customary cosmetic auxiliaries, for example softeners, such as glycerol and glycol; emollients; perfumes; surfactants; UV absorbers; dyes; antistats; combability improvers; preservatives; and antifoams.
- 15 If the compositions according to the invention are formulated as hairsprays, they comprise a sufficient amount of a propellant, for example a low-boiling hydrocarbon or ether, such as propane, butane, isobutane or dimethyl ether. Propellants which can be
- 20 used are also compressed gases, such as nitrogen, air or carbon dioxide. The amount of propellant can be kept low so as not to raise the VOC content unnecessarily. In general, the amount is then no more than 55% by weight based on the total weight of the composition. However, higher VOC contents of 85% by weight and
- 25 above are also possible if desired.

The polyurethanes described above can also be used in the compositions in combination with other hair polymers. Such polymers are, in particular:

- 30 - nonionic, water-soluble or water-dispersible polymers or oligomers, such as polyvinylcaprolactam, e.g. Luviskol Plus (BASF), or polyvinylpyrrolidone and its copolymers, in particular with vinyl esters, such as vinyl acetate, e.g.
- 35 Luviskol VA 37 (BASF); polyamides, e.g. those based on itaconic acid and aliphatic diamines, as described, for example, in DE-A-43 33 238; polyvinyl alcohols and derivatives thereof; polymers based on cellulose;
- 40 - amphoteric or zwitterionoic polymers such as the octylacrylamide/methylmethacrylate/tert-butylaminoethyl methacrylate/2-hydroxypropyl methacrylate copolymers obtainable under the names Amphomer® (National Starch), and zwitterionic polymers as disclosed, for example in German
- 45 Patent applications DE 39 29 973, DE 21 50 557, DE 28 17 369 and DE 37 08 451. Acrylamidopropyltrimethylammonium chloride/acrylic acid and methacrylic acid copolymers and

38

- alkali metal and ammonium salts thereof are preferred zwitterionic polymers. Other suitable zwitterionic polymers are methacroylethylbetaine/methacrylate copolymers, which are available commercially under the name Amersette® (AMERCHOL), and copolymers of hydroxyethyl methacrylate, methyl methacrylate, N,N-dimethylaminoethyl methacrylate and acrylic acid (Jordapon®);
- 5
- anionic polymers, such as vinyl acetate/crotonic acid copolymers, as are commercially available, for example under the names Resyn® (NATIONAL STARCH), Luviset® (BASF) and Gafset® (GAF), and vinylpyrrolidone/vinylacrylate copolymers, obtainable for example under the tradename Luviflex® (BASF). A preferred polymer is the vinyl pyrrolidone/acrylate terpolymer available under the name Luviflex® VBM-35 (BASF). Acrylic acid/ethyl acrylate/N-tert-butylacrylamide terpolymers, which are marketed, for example under the name Ultrahold® strong (BASF), and Luvimer® (BASF, terpolymer of t-butyl acrylate, ethyl acrylate and methacrylic acid), sodium sulfonate-containing polyamides or sodium sulfonate-containing polyesters, or
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- 15
- 20
- cationic (quaternized) polymers, e.g. cationic polyacrylate copolymers based on N-vinyl lactams and derivatives thereof (N-vinylpyrrolidone, N-vinylcaprolactam etc.) and customary cationic hair-conditioning polymers, e.g. Luviquat® (copolymer of vinylpyrrolidone and vinylimidazolium methochloride), Luviquat® Hold (copolymer of quaternized N-vinylimidazole, N-vinylpyrrolidone and N-vinylcaprolactam), Merquat® (polymer based on dimethyldiallylammonium chloride), Gafquat® (quaternary polymers formed by reacting polyvinylpyrrolidone with quaternary ammonium compounds), polymer JR (hydroxyethylcellulose with cationic groups), polyquaternium grades (CTFA names) etc., chitosan and chitosan derivatives;
- 25
- 30
- 35
- nonionic, siloxane-containing, water-soluble or -dispersible polymers, e.g. polyether siloxanes, such as Tegopren® (Goldschmidt) or Belsil® (Wacker).
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- The polymers according to the invention can be used as a mixture with an amide-containing hair polymer. These include, for example, the polyurethanes described in DE-A-42 25 045, the above-described vinylpyrrolidone/acrylate terpolymers and acrylic acid/ethyl acrylate/N-tert-butylacrylamide terpolymers (e.g. Ultrahold® strong from BASF AG), the above-described amide-containing amphoteric polymers (e.g. Amphomer®) and in
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particular copolymers which have a proportion of amide-containing monomers, such as N-vinyl lactams, of at least 30% by weight (e.g. Luviskol®plus and Luviskol®VA37 from BASF AG).

- 5 The other hair polymers are preferably present in amounts up to 10% by weight, based on the total weight of the composition.

A preferred hair-treatment composition comprises:

- 10 a) from 0.5 to 20% by weight, preferably from 1 to 10% by weight, of at least one water-soluble or -dispersible polyurethane according to the invention,
- 15 b) from 50 to 99.5% by weight, preferably from 55 to 99% by weight, of a solvent chosen from water and water-miscible solvents, preferably C₂-C₅-alcohols, in particular ethanol, and mixtures thereof,
- 20 c) from 0 to 70% by weight, preferably from 0.1 to 50% by weight, of a propellant, preferably chosen from dimethyl ether and alkanes, such as, for example, propane/butane mixtures,
- 25 d) from 0 to 10% by weight, preferably from 0.1 to 10% by weight, of at least one water-soluble or -dispersible hair polymer which is different from a),
- 30 e) from 0 to 0.5% by weight, preferably from 0.001 to 2% by weight, of at least one water-soluble or water-dispersible silicone compound,
- 35 f) from 0 to 1% by weight, preferably 0.0001 to 0.5% by weight, of at least one compound chosen from esters and amides of saturated and mono- or polyunsaturated C₅- to C₃₀-carboxylic acids, saturated and mono- or polyunsaturated C₈- to C₃₀-alcohols and mixtures thereof,

and customary additives.

- 40 The composition according to the invention can comprise, as component d), at least one other water-soluble or -dispersible hair polymer. The proportion of this component is then generally from about 0.1 to 10% by weight, based on the total weight of the composition. Preference is given in this connection to using
- 45 water-soluble or water-dispersible polyurethanes which do not contain siloxane groups in copolymerized form.

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The composition according to the invention can comprise, as component e), at least one nonionic, siloxane-containing, water-soluble or water-dispersible polymer, chosen in particular from the above-described polyether siloxanes. The proportion of
5 this component is then generally from about 0.001 to 2% by weight, based on the total weight of the composition.

The composition according to the invention can comprise, as additional component, at least one water-insoluble silicone, in
10 particular a polydimethylsiloxane, e.g. the Abil® grades from Goldschmidt. The proportion of this component is then generally from about 0.0001 to 0.2% by weight, preferably from 0.001 to 0.1% by weight, based on the total weight of the composition.

15 The composition according to the invention can additionally comprise, where appropriate, an antifoam based, for example, on silicone. The amount of the antifoam is then generally up to about 0.001% by weight, based on the total amount of the composition.

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The composition according to the invention preferably comprises, as component f), at least one ester of the formula $R^{20}-CO-OR^{21}$, in which R^{20} is a straight-chain or branched C_5- to $C_{30}-$, preferably $C_{10}-$ to C_{20} -alkyl or -alkenyl radical, where the alkenyl radical
25 can have 1, 2, 3 or 4 nonadjacent double bonds. R^{21} is preferably a straight-chain or branched C_1- to $C_{30}-$, in particular C_5- to C_{22} -alkyl radical or a straight-chain or branched C_6- to $C_{30}-$, in particular C_8- to C_{22} -alkenyl radical, which can have 1, 2, 3 or 4 nonadjacent double bonds.

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Preference is given to using the esters of caproic acid, caprylic acid, 2-ethylhexanoic acid, capric acid, lauric acid, isotridecanoic acid, myristic acid, palmitic acid, palmoleic acid, stearic acid, isostearic acid, oleic acid, elaidic acid,
35 petroselic acid, linoleic acid, linolenic acid, elaeostearic acid, arachidic acid, gadoleic acid, behenic acid and erucic acid, and mixtures thereof, with lauryl alcohol, isotridecyl alcohol, myristyl alcohol, cetyl alcohol, palmoleyl alcohol, stearyl alcohol, isostearyl alcohol, oleyl alcohol, elaidyl
40 alcohol, petroseliny alcohol, linolyl alcohol, linolenyl alcohol, elaeostearyl alcohol, arachidyl alcohol, gadoley alcohol, behenyl alcohol, erucyl alcohol and brassidyl alcohol, and mixtures thereof. Preference is given to using esters which have, in the fatty acid and fatty alcohol components together, at
45 least 24, preferably at least 30 carbon atoms and optionally a

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double bond. Typical examples are oleyl erucate, erucyl oleate, behenyl oleate and cetearyl oleate.

Also preferred as component f) are amides of the formula
5 $R^{20}-CO-NR^{22}R^{23}$, where R^{20} can have the meanings given above, and R^{22} and R^{23} independently of one another are hydrogen, C_1 - to C_{12} -alkyl or C_5 - to C_8 -cycloalkyl.

Also preferred as component f) are saturated, and mono- or
10 polyunsaturated alcohols. Suitable C_8 - to C_{30} -alkyl radicals are those mentioned above. The alcohols can be used individually or as mixtures. Such alcohols and alcohol mixtures are obtainable, for example, by hydrogenation of fatty acids from natural fats and oils or of synthetic fatty acids, e.g. from the catalytic
15 oxidation of paraffins. Suitable alcohols and alcohol mixtures are also obtainable by hydroformylation of olefins with simultaneous hydrogenation of the aldehydes, mixtures of straight-chain and branched primary alcohols (oxo alcohols) generally resulting. Suitable alcohols and alcohol mixtures are
20 also obtainable by partial oxidation of n-paraffins by known processes, giving predominantly linear secondary alcohols. Also suitable are the essentially primary, straight-chain and even-numbered Ziegler alcohols.

25 Preferred alcohols f) are the Guerbet alcohols. Guerbet alcohols which are preferably used as component f) are preferably obtained by base-catalyzed self-condensation of linear and/or branched alcohols having 6 to 22 and preferably 8 to 18 carbon atoms. A review on this topic can be found in A. J. O'Lennick in Soap
30 Cosm. Chem. Spec. (April) 52 (1987). Typical examples are condensation products of technical-grade fatty alcohol cuts having 8 to 10 or 16 to 18 carbon atoms.

The compounds given above as component f) can be used
35 individually or as mixtures. The cosmetic compositions according to the invention which comprise component f) generally have good performance properties, such as, for example, good flexibility and a pleasant feel, even without the use of silicone-containing components.

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In addition to the abovementioned components, the composition according to the invention preferably comprises:

g) from 0 to 40% by weight, preferably from 0.1 to 35% by
45 weight, of at least one surfactant,

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- h) from 0 to 5% by weight, preferably from 0.05 to 4% by weight, of at least one dye and/or UV absorber,
- i) from 0 to 3% by weight, preferably from 0.05 to 2.5% by weight, of at least one salt,
- k) from 0 to 3% by weight, preferably from 0.05 to 2.5% by weight, of at least one thickener,
- 10 and optionally other customary additives. These are then each generally present in an amount of from about 0 to 0.2% by weight, preferably from 0.001 to 0.2% by weight based on the total weight of the composition.
- 15 The compositions according to the invention have the advantage that on the one hand they impart the desired hold to hair and the polymers can be washed out easily (are redispersible), and on the other hand the hair remains elastic.
- 20 Advantageously, the polyurethanes according to the invention are also suitable as components in hair-treatment compositions which additionally comprise at least one other traditional hair polymer. With these mixtures, too, better flexibilities are generally achieved than for the corresponding polymers or
- 25 mixtures which do not contain the polyurethanes according to the invention. The polyurethanes according to the invention are therefore also suitable for improving the elasticity of conventional hair-setting compositions. These then generally impart very good flexibility and suppleness to the hair.
- 30 The invention is illustrated in more detail by reference to the nonlimiting examples below.

I. Preparation of oligomers

Oligomer O1:

Preparation of a polyurethanediol from hexamethylene diisocyanate and neopentyl glycol

- 40 In a four-necked flask, which was fitted with stirrer, dropping funnel, thermometer, reflux condenser and equipment for working under nitrogen, 624 g (6 mol) of neopentyl glycol and 0.3 g of tetrabutyl orthotitanate were dissolved in 490 g of methyl ethyl
- 45 ketone with heating to a temperature of about 50°C and with stirring. Then, with stirring, 840 g (5 mol) of hexamethylene diisocyanate were added dropwise, and the reaction temperature

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increased. The reaction mixture was then stirred for 2 hours under reflux and then cooled to room temperature with stirring. This gave a clear, high-viscosity 75% strength by weight solution of a polyurethane diol having an OH number of about 75 and a number-average molecular weight of about 1500 g/mol.

Oligomer O2:

Preparation of a polyurethane based on polytetrahydrofuran

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A four-necked flask, which was fitted with stirrer, dropping funnel, thermometer, reflux condenser and equipment for working under nitrogen, was charged with 650 g (1 mol) of polytetrahydrofuran ($M_n = 650$ g/mol) and 0.1 g of tetrabutyl orthotitanate, and the mixture was heated to about 50°C with stirring. Then, with stirring, 109.5 g (0.65 mol) of hexamethylene diisocyanate were added dropwise, and the reaction temperature increased. The reaction mixture was stirred for a further 3 hours at 80°C. Cooling to room temperature gave a wax-like product having an OH number of about 50 with a number-average molecular weight of about 2250 g/mol.

Oligomer O2 can also be prepared analogously to the preparation procedure for oligomer O1, i.e. in a solvent, such as methyl ethyl ketone.

Oligomer O3:

Preparation of a polyurethane based on a polyesterdiol

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The polycondensation of 3.5 mol of sebacic acid and 4.5 mol of 1,6-hexanediol gave a hydroxyl-containing polyesterdiol having a number-average molecular weight of about 1150 g/mol. Analogously to the preparation procedure for oligomer O2, 1 mol of the polyesterdiol and 0.65 mol of hexamethylene diisocyanate were reacted. This gave a hard wax-like product having an OH number of about 30 and a number-average molecular weight of about 3700 g/mol.

Oligomer O4 was prepared analogously to oligomer O3. The starting materials used and the amounts thereof are given in Table 1 below.

Oligomer O5:

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Preparation of a polyurethane based on a polysiloxanediol

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According to the general preparation procedure for oligomer O1, 1 mol of polysiloxanediol ($M_n = 900$ g/mol, Tegomer® H-Si 2122 from Goldschmidt) and 0.65 mol of hexamethylene diisocyanate were reacted in methyl ethyl ketone.

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The preparation of oligomers of this type can also be carried out according to the general procedure for oligomer O2, i.e. without the addition of a solvent.

10 Oligomer O6:

Preparation of a polyurethane based on a polysiloxanediamine

15 Analogously to the preparation procedure for oligomer O1, 1 mol of polysiloxanediamine ($M_n = 900$ g/mol, Tegomer® A-Si 2122 from Goldschmidt) and 0.65 mol of hexamethylene diisocyanate were reacted in methyl ethyl ketone at a temperature of about 30°C and without the addition of a catalyst.

20 Oligomer O7:

Preparation of a hydroxyl-containing reaction product of a polyurethanediol with a dimer fatty acid

25 In a four-necked flask, which was fitted with stirrer, dropping funnel, thermometer, reflux condenser and equipment for working under nitrogen, in accordance with the general preparation procedure for oligomer O1, a polyurethanediol was prepared from 2 mol of 1,6-hexanediol and 1 mol of hexamethylene diisocyanate.
30 The reflux condenser was then replaced by a descending condenser. Under a nitrogen atmosphere, 0.65 mol of a dimer fatty acid were added and the reaction mixture was heated, the methyl ethyl ketone being distilled off firstly at a temperature of from 80 to 110°C. After a further temperature increase to 160°C, the reaction
35 mixture was stirred for a further 3 hours, and the reaction temperature then increased by about 20°C per hour until it had reached about 210°C. After a further 5 hours at about 210°C, the acid number was less than 2. The mixture was left to cool to room temperature, giving a yellow, almost clear wax having an OH
40 number of about 48 and a number-average molecular weight of about 2300 g/mol.

Oligomer O8:

45 Preparation of a hydroxyl-containing reaction product of a polyurethane with sebacic acid

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Analogously to the general preparation procedure for the reaction product 07, a polyurethanediol was firstly prepared from 2 mol of 1,6-hexanediol and 1 mol of hexamethylene diisocyanate, and then reacted with 0.65 mol of sebacic acid.

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Table 1: Oligomers

Oligomer No.	HDI ¹⁾ [mol]	NPG ²⁾ [mol]	1,6-HD ³⁾ [mol]	Sebacic acid [mol]	Dimer fatty acid ⁴⁾ [mol]	Polysiloxane-diamine/diol ⁵⁾ [mol]	Poly-(THF) ⁶⁾ [mol]
O1	5	6	-	-	-	-	-
O2	0.65	-	-	-	-	-	1
O3	0.65	-	4.5	3.5	-	-	-
O4	0.65	-	2	-	3	-	-
O5	0.65	-	-	-	-	1 (diol)	-
O6	0.65	-	-	-	-	1 (diamine)	-
O7	1	-	2	-	0.65	-	-
O8	1	-	2	0.65	-	-	-

1) Hexamethylene diisocyanate

2) Neopentyl glycol

3) 1,6-Hexanediol

4) Dimer fatty acid, Empol® 1008 from Henkel

5) Polysiloxanediol, $M_n = 900$ g/mol (Tegomer® H-Si 2122 from Goldschmidt)Polysiloxanediamine, $M_n = 900$ g/mol (Tegomer® A-Si 2122 from Goldschmidt)6) Polytetrahydrofuran, $M_n = 650$ g/mol

II. Preparation of polymers

II.1: Oil-soluble polymers P9 to P11

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The polymers P9 to P11 were prepared analogously to the preparation procedure for oligomer O3 from starting materials according to Table 2.

10 II.2: Water-soluble polymers P12 and P13

The polymers P12 and P13 were prepared without a diluent analogously to the preparation procedure for oligomer O2 from starting materials according to Table 2.

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Table 2: Polymers

Polymer No.	HDI 1) [mol]	DMPA 2) [mol]	PE-diol 3) [mol]	Poly-siloxane-diol 4) [mol]	Poly-(THF) 5) [mol]	PEG-1500 6) [mol]
P9	9.5	-	10	-	-	-
P10	9.5	-	9	1	-	-
P11	9.5	-	9	-	1	-
P12	9.5	-	-	-	-	10
P13	9.5	1.5	-	-	-	8.5

- 1) hexamethylene diisocyanate
- 2) dimethylolpropanoic acid
- 3) polyesterdiol from dimer fatty acid and 1,6-hexanediol, $M_n = 2\ 000\text{ g/mol}$
- 4) polysiloxanediol, $M_n = 900\text{ g/mol}$ (Tegomer® H-Si 2122 from Goldschmidt)
- 5) polytetrahydrofuran, $M_n = 1\ 000\text{ g/mol}$
- 6) dealkylated polyethylene glycol, $M_n = 1\ 500\text{ g/mol}$

Performance examples (oligomers O1 to O8 and oil-soluble polymers P9 to P11):

- 5 To prepare formulations of the abovementioned oligomers and polymers, these are mixed with a C₁₂- to C₁₅-alkyl benzoate (Finsolv® TN) in an amount according to Table 3 and the properties of the resulting mixtures are assessed.

10 Table 3:

Example No.	Oil component		
	20% by wt.	10% by wt.	5% by wt.
O1	insoluble	insoluble	insoluble
15 O2	virtually clear viscous oil	virtually clear viscous oil	clear viscous oil
O3	solid, slightly opaque wax	solid, virtually clear wax	just solid, virtually clear wax
20 O4	solid clear wax	solid clear wax	clear high-viscosity oil
25 O5	virtually clear, viscous oil, separates into two phases upon standing	virtually clear, viscous oil, separates into two phases upon standing	virtually clear, viscous oil, separates into two phases upon standing
30 O6	opaque viscous oil, separates into two phases upon standing	slightly opaque viscous oil, separates into two phases upon standing	virtually clear, viscous oil, separates into two phases upon standing
O7	very solid, clear wax	solid clear wax	clear high-viscosity oil
35 O8	very solid, clear wax	solid, slightly opaque wax	virtually clear high-viscosity oil
P9	very solid, clear wax	solid, clear wax	just solid, clear wax
40 P10	just solid, clear wax	just solid, clear wax; becomes oily on shaking	clear viscous oil
45 P11	solid, virtually clear wax	just solid, virtually clear wax; becomes oily upon shaking	clear viscous oil

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Formulation examples for use in skin cosmetics (oligomers O1 to O8 and oil-soluble polymers P9 to P11):

Table 4:

5	Substance	Field of use			
		Oil base	Ointment base	Wax base	Stick base
10	Oligomer/polymer from Ex. No./ [% by wt.]	O4, O7, O8, P9, P10, P11/ 5	O4, O7, O8, P9/ 5	O4, O7, P9/ 10	O4, O7, O8, P9/ 30
	Paraffin oil [% by wt.]	10	-	-	-
15	Cosmetic oil: Finsolv® TN ¹⁾ Miglyol ²⁾ Castor oil [% by wt.]	60 - -	Fins. &/or Migl. 30 -	65 - 15	60 - 10
20	Paraffin wax ³⁾	-	5	5	-
	Vaseline	20	50	5	-
	Beeswax ⁴⁾	5	5	-	-
	Cetyl alcohol	-	5	-	-

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1) C₁₂-C₁₅-alkyl benzoate

2) neutral oil, triglyceride of saturated vegetable fatty acids

3) homopolymeric polyethylene wax (Luwax® A, BASF),
copolymeric polyethylene wax, acrylic acid copolymer (Luwax® EAS, BASF),
copolymeric polyethylene wax, vinyl acetate copolymer (Luwax® EVA, BASF)
and mixtures thereof

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4) e.g. Berry Wax and/or Ultrabee WD (both Kahl, Germany)

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The formulations can comprise further components chosen from color pigments, oil-soluble vitamins, oil-soluble UV absorbers, perfume, essential oils, preservatives, etc.

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Examples of emulsifier-free emulsions (oligomers and oil-soluble polymers):

5	Oil phase:	% by wt.	Chemical name/ CTFA name:
	Finsolv® TN	18	C ₁₂ -C ₁₅ -alkyl benzoate
	Oligomer/polymer O4, O7, O8, P9, P10, P11	2	
10	Nip Nip®, Nipa Laboratories Ltd. USA	0.1	methyl- and propyl-4-hydroxybenzoate (7:3)
15	Water phase:	% by wt.	
	Water	79.2	
	Carbopol 940	0.4	Polyacrylic acid (Goodrich)
	Mowiol 4/88	0.2	Polyvinyl alcohol (degree of saponification 88%, Hoesch)
20	Germall 115	0.1	Imidazolidinylurea

Preparation of the emulsifier-free emulsions

- 25 To prepare the emulsifier-free emulsions, the components for oil and water phase are weighed separately and the oil phase is homogenized at about 100°C and the water phase is homogenized at about 60°C. The heated oil phase (20-80°C) is then slowly added, with stirring, to the likewise optionally heated water phase
- 30 (0-80°C). The higher the temperatures of the water and oil phase, the finer the resulting emulsions. Neutralization with 2-amino-2-methylpropanol (50% strength in water) to pH 7.5 to 8.5 gives stable emulsions.

35 Examples of creams (oligomers and oil-soluble polymers):

40	Oil phase:	% by wt.	Chemical name/CTFA name:
	Paraffin oil	4.5	
	Cremophor® A6 (BASF AG)	2.5	Ceteareth-6 (stearyl alcohol ethoxylate)
45	Cremophor® A6 (BASF AG)	2.5	Ceteareth-25 (fatty alcohol ethoxylate)
	Cetyl alcohol	3.5	
	Glycerol monostearate s.e.	2.5	Glyceryl stearate
	Isopropyl palmitate	2.0	
	Luvitol® EHO (BASF AG)	6.2	Cetearyl octanoate

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Oligomer/Polymer O4, O7, O8, P9, P10, P11	1.1	
Nip Nip®, Nipa Laboratories Ltd. USA	0.1	methyl- and propyl-4-hydroxybenzoate (7:3)

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Water phase:	% by wt.	
Water	75.0	
Germall 115	0.1	Imidazolidinylurea

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	Oil phase:	% by wt.	Chemical name/CTFA name:
	Paraffin oil	4.5	
15	Cremophor® A6 (BASF AG)	2.5	Ceteareth-6 (stearyl alcohol ethoxylate)
	Cremophor® A6 (BASF AG)	2.5	Ceteareth-25 (fatty alcohol ethoxylate)
	Luwax® A	3.6	
20	Glycerol monostearate s.e.	2.5	Glyceryl stearate
	Isopropyl palmitate	2.0	
	Luvitol® EHO (BASF AG)	6.2	Cetearyl octanoate
	Oligomer/Polymer O4, O7, O8, P9, P10, P11	1.0	
25	Nip Nip®, Nipa Laboratories Ltd. USA	0.1	Methyl- and Propyl-4-hydroxybenzoate (7:3)

	Water phase:	% by wt.	
30	P12 or P13	1.0	
	Water	74.0	
	Germall 115	0.1	Imidazolidinylurea

35 Preparation:

Weigh and homogenize separately, with stirring, the oil phases and water phase at a temperature of about 80°C. Slowly stir in the water phase into the oil phase. Cool slowly to room temperature
40 with stirring.

Examples for use in hair cosmetics (water-soluble polymers 12 and 13):

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Gel with water-soluble polymers and polyvinyl alcohol

	Composition	% by wt.
5	a) Aqueous solution of Carbopol 940 (1% strength) ¹⁾	100
	b) Aqueous solution of Polymer 12 or 13 (10% strength)	50
	c) Aqueous solution of Mowiol 4/88 (20% strength) ²⁾	49
10	d) AMP solution (10% strength) ³⁾	1

1) Carbopol 940: polyacrylic acid (Goodrich)

2) Mowiol 4/88: Polyvinyl alcohol (degree of saponification 88%,
15 Hoesch)

3) AMP: aminomethylpropanol

Preparation:

20 A mixture of b), c) and d) is brought to a temperature of about 40°C with stirring. An aqueous polyacrylic acid solution is then added, and stirring is continued until the mixture produces a slightly opaque homogeneous solution. The solution is cooled to a temperature of about 25°C with stirring. The addition of
25 aminomethylpropanol gives a clear gel.

III. Polyurethane preparation

Preparation method A:

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Example 3

In a stirred apparatus, which was fitted with stirrer, dropping funnel, thermometer, reflux condenser and equipment for working
35 under nitrogen, 600 g (0.3 mol) of oligomer O1, 600 g (0.4 mol) of a polyesterdiol ($M_n = 1\,500$ g/mol, prepared from isophthalic acid, adipic acid, neopentyl glycol and cyclohexanedimethylol), 124.8 g (1.2 mol) of neopentyl glycol, 375.2 g (2.8 mol) of dimethylolpropanoic acid and 0.5 g of tetrabutyl orthotitanate
40 were dissolved in 760 g of methyl ethyl ketone with heating to a temperature of about 80°C and with stirring. After everything had dissolved, the reaction mixture was cooled to about 50°C. Then, with stirring, 1111 g (5 mol) of isophorone diisocyanate were added dropwise, and the reaction temperature increased. The
45 reaction mixture was then stirred under reflux until the isocyanate group content of the mixture remained virtually constant, and then cooled to room temperature with stirring.

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Then, to convert the free isocyanate groups, 276 g (3.1 mol) of 2-amino-2-methyl-1-propanol was added as an aqueous solution to the mixture at a temperature of about 40°C in order to neutralize the mixture to 100%. The flexibility properties of the resulting 5 polymers are given in Table 5. Distilling off the solvent under reduced pressure at 40°C gives an aqueous (micro)dispersion. Pulverulent products can be obtained by spraydrying.

The polymers C1, 2, 4-6 and 11 were prepared analogously to this 10 preparation procedure.

All carboxylic acid-containing polyurethanes were neutralized to 100% with 2-amino-2-methyl-1-propanol. The cationic polyurethanes 11 and 12 were neutralized with lactic acid, and polyurethane 13 15 was quaternized with dimethyl sulfate.

Preparation procedure B:

Example 7

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In a stirred apparatus, which was equipped with stirrer, dropping funnel, thermometer, reflux condenser and equipment for working under nitrogen, 600 g (0.4 mol) of a polyesterdiol ($M_n = 1\ 000$ g/mol, prepared from isophthalic acid, adipic acid, 25 neopentyl glycol and cyclohexanedimethylol), 187.2 g (1.8 mol) of neopentyl glycol and 0.5 g of tetrabutyl orthotitanate were dissolved in 350 g of methyl ethyl ketone with heating to a temperature of about 50°C and with stirring. Then, with stirring, 252 g (1.5 mol) of hexamethylene diisocyanate were added 30 dropwise, and the reaction temperature increased. The reaction mixture was stirred under reflux for about 2 hours and then cooled to room temperature. 124.8 g (1.2 mol) of neopentyl glycol, 375.2 g (2.8 mol) of dimethylolpropanoic acid and 200 g of methyl ethyl ketone were then added to the reaction mixture 35 and dissolved with heating to a temperature of about 80°C and with stirring. After everything had dissolved, the reaction mixture was cooled to about 50°C. Then, with stirring, a mixture of 222 g (1 mol) of isophorone diisocyanate and 672 g (4 mol) of hexamethylene diisocyanate were added dropwise, and the reaction 40 temperature increased. The reaction mixture was then stirred under reflux until the isocyanate group content remained virtually constant, and was then cooled to room temperature with stirring. Then, to convert the free isocyanate groups, 276 g (3.1 mol) of 2-amino-2-methyl-1-propanol were added as an aqueous 45 solution to the mixture at a temperature of about 40°C in order to neutralize the mixture to 100%. Distilling of the solvent under

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reduced pressure at 40°C gives an aqueous (micro)dispersion. Pulverulent products can be obtained by spraydrying.

Polymers 8-10, 12 and 13 were prepared analogously to this 5 preparation procedure.

The performance properties were assessed by the awarding of grades for flexibility by independent experts. The grading table is given in Table 6.

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Table 5: Polyurethanes

Example No.	P(ester-diol) [mol]	Poly-THF [mol]	Polysiloxane-diamine [mol]	Oligomer O1 [mol]	HDI [mol]	NPG [mol]	DMPA [mol]	MDEA [mol]	IPDI [mol]	Preparation method	Flexibility grade
C1	0.7	-	-	-	-	1.2	2.8	-	5	A	4
2	-	-	-	0.7	-	1.2	2.8	-	5	A	3
3	0.4	-	-	0.3	-	1.2	2.8	-	5	A	3
4	0.4	-	-	0.3	1.5	1.2	2.8	-	3.5	A	3
5	0.4	-	-	0.3	3	1.2	2.8	-	2	A	2-3
6	-	-	-	0.7	3	1.2	2.8	-	2	A	2
7	0.4 *)	-	-	-	1.5 *)4	1.8 *)	2.8	-	1	B	1-2
8	-	-	-	-	3.5 *)4	4.2 *)	2.8	-	1	B	1-2
9	0.4 *)	-	0.1 *)	-	1.8 *)4	1.8 *)	3.0	-	1	B	1-2
10	0.4 *)	-	-	-	2.8 *)4	1.8 *)	3.0	1	1	B	1-2
11	-	0.4	-	0.3	2.2	1.2	-	3.0	3	A	1-2

12	-	0.4 *)	-	-	1.8 *)3	1.8 *)	-	3.0	2	B	1-2
13	-	0.4 *)	0.1 *)	-	1.8 *)4	1.8 *)	-	3.2	1	B	1

*) The components thus characterized are reacted together in a first reaction step.

P(esterdiol): Polyesterdiol of isophthalic acid, adipic acid, neopentyl glycol, dimethanoldiisocyanate, hexane; MW \approx 1500 g/mol

Poly-THF: Polytetrahydrofuran, $M_n = 1\ 000$ g/mol

Polysiloxanediamine: $M_n = 900$ g/mol (Tegomer® A-Si 2122 from Goldschmidt)

HDI: Hexamethylene diisocyanate
 NPG: Neopentyl glycol
 DMPA: Dimethanolpropanoic acid
 MDEA: N-Methyldiethanolamine
 IPDI: Isophorone diisocyanate
 AMP: Amino-2-methyl-propanol

Table 6: Flexibility

<u>Grade</u>	<u>Flexibility</u>
5 1	very flexible
2	flexible
3	moderately flexible
4	brittle

10 Application examples

Examples 14 to 25

Aerosol hairspray formulations with a VOC content of 97% by weight:

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Polyurethane as in Ex. 2-13	3.00% by weight
Ethanol	57.00% by weight
Dimethyl ether	34.96% by weight
Perfume, additives	q.s.

20 (inc. erucic esters)

Examples 26 to 37

Compact aerosol hairspray formulations with a VOC content of 80% by weight:

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Polyurethane as in Ex. 2-13	5.00% by weight
Ethanol	40.00% by weight
Dimethyl ether	34.96% by weight
Water	15.00% by weight

30 Perfume, additives

q.s.

Examples 38 to 49

Hairspray formulations with a VOC content of 55% by weight:

35 Polyurethane as in Ex. 2-13

3.00% by weight

Ethanol

20.00% by weight

Water

42.00% by weight

Dimethyl ether

34.96% by weight

Perfume, additives

q.s.

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Examples 50 to 61

Pump hairspray:

Polyurethane as in Ex. 2-13

5.00% by weight

45 Ethanol

54.96% by weight

Water

40.00% by weight

59

Perfume, additives

q.s.

Examples 62 to 73

Foam conditioner

:[% by weight]

5	Polymer 2-13 (25% strength aqueous solution)	20.00
	Cremophor® A25 ⁷⁾	0.20
	Comperlan® KD ⁸⁾	0.10
	Water	69.70
10	Propane/butane	9.96
	Perfume, preservatives	q.s.

7) CTFA Name: Ceteareth 25, BASF AG, reaction product of fatty alcohol and ethylene oxide

15 8) CTFA Name: Cocamide DEA, Henkel, coconut fatty acid amide

To prepare the foam conditioner, the components are weighed in and dissolved with stirring. They are then transferred to a dispenser and the propellant is added.

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Examples 74 to 85

Aerosol hairspray with a VOC content of 80% by weight based on polyurethane oligomers

25	Polymer as in Ex. 2-13	5.00% by weight
	Oligomer 2-8	0.10% by weight
	Ethanol	40.00% by weight
	Dimethyl ether	34.96% by weight
	Water	14.90% by weight
30	Perfume, additives	q.s.

Examples 86 to 88

Conditioner shampoo:

[% by weight]

35 A)	Texapon® NSO 28% strength ⁹⁾	50.00
	Comperlan® RD	1.00
	Polymer 11-13 (25% strength aqueous solution)	20.00
	Perfume oil	q.s.

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B)	Water	27.5
	Sodium chloride	1.5
	Preservative	q.s.

45 9) Sodium lauryl sulfate, Henkel

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To prepare the conditioner shampoos, components A) and B) are weighed in separately and dissolved with mixing. Phase B) is then slowly added to phase A).

5 Examples of applications in skin cosmetics

Examples 89 to 95

O/W creams

10	Oil phase:	% by weight	CTFA Name:
	Oligomer 2-8	1.1	
15	Cremophor® A6 (BASF AG)	3.5	Ceteareth-6 (stearyl alcohol ethoxylate)
	Cremophor® A25 (BASF AG)	3.5	Ceteareth-25 (fatty alcohol ethoxylate)
	Glycerol monostearate s.e.	2.5	Glyceryl stearate
20	Paraffin oil	7.5	
	Cetyl alcohol	3.5	
	Luvitol® EHO (BASF AG)	3.2	Cetearyl octanoate
	Nip-Nip®, Nipa Laboratories Ltd., USA	0.1	Methyl and Propyl 4-hydroxybenzoate (7:3)
25	Water phase:	% by weight	
	Water	75.0	
30	Germall II, Sutton Laboratories Inc., USA	0.1	Diazolidinylurea

To prepare the creams, the components for the oil and water phase are weighed separately and homogenized at 80°C. The water phase is then slowly added to the oil phase with stirring. The mixture is then left to cool to room temperature with stirring.

Examples 96 to 107

O/W creams

40	Oil phase:	% by weight	CTFA Name:
	Cremophor® A6 (BASF AG)	3.5	Ceteareth-6 (stearyl alcohol ethoxylate)
45	Cremophor® A25 (BASF AG)	3.5	Ceteareth-25 (fatty alcohol ethoxylate)
	Glycerol monostearate s.e.	2.5	Glyceryl stearate

61

5	Paraffin oil	7.5	
	Cetyl alcohol	3.5	
	Luvitol® EHO (BASF AG)	3.2	Cetearyl octanoate
	Nip-Nip®, Nipa Laboratories Ltd., USA	0.1	Methyl and Propyl 4-hydroxybenzoate (7:3)

10	Water phase:	% by weight	
	Polymer 2-13	1.5	
	Water	74.6	
	Germall II, Sutton Laboratories Inc., USA	0.1	Diazolidinylurea

15 To prepare the creams, the components for the oil and water phase are weighed separately and homogenized at 80°C. The water phase is then slowly added to the oil phase with stirring. The mixture is then left to cool to room temperature with stirring.

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Translation of amended sheets annexed to the IPER

62

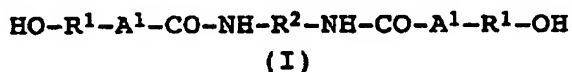
We claim:

1. A cosmetic composition comprising:
 - at least one oligomer of
 - A) at least one aliphatic diisocyanate,
 - B) at least one compound having at least two groups which are reactive toward isocyanate groups, which is chosen from
 - B1) aliphatic and cycloaliphatic polyols, polyamines and/or aminoalcohols,
 - B2) polyetherols and/or diaminopolyethers,
 - B3) polysiloxanes having at least two active hydrogen atoms per molecule,
 - B4) polyester polyols,
 - and mixtures thereof, and
 - C) optionally at least one dicarboxylic acid and/or hydroxycarboxylic acid,
- where the oligomer comprises, per molecule, at least two urethane and/or urea groups and additionally at least two further functional groups chosen from hydroxyl, primary and/or secondary amino groups, and where oligomers from components A) and B) have a molecular weight in the range from 500 to 7 000 and oligomers of components A), B) and C) have a molecular weight in the range from 500 to 10 000.
2. A composition as claimed in claim 1, comprising at least one oligomer which comprises, in incorporated form, at least one component B4) chosen from esters of di- or polyhydric alcohols with at least one carboxylic acid, the carboxylic acid being chosen from
 - cyclic and acyclic dicarboxylic acids, obtained by dimerization of unsaturated C₆- to C₃₀-carboxylic acids,
 - aliphatic, cycloaliphatic and aromatic C₈- to C₃₀-dicarboxylic acids,
 - C₈- to C₃₀-hydroxycarboxylic acids
- and mixtures thereof.

Translation of amended sheets annexed to the IPER

63

3. A composition as claimed in claim 1, comprising at least one oligomer from the components A), B1) and C).
4. A composition as claimed in claim 3, where the oligomer is obtainable by reacting at least one compound from the component A) and B1) of the formula I



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in which

- R¹ is C₂- to C₁₂-alkylene, C₅- to C₈-cycloalkylene or arylene, where alkylene radicals may be interrupted by one or two C₅- to C₈-cycloalkylene or arylene radicals,
- R² is a radical derived from an aliphatic, cycloaliphatic or aromatic diisocyanate following removal of the isocyanate groups,
- A¹ is O or NR³, where R³ is hydrogen, C₁- to C₆-alkyl or C₅- to C₈-cycloalkyl,

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with at least one compound of component C), which is chosen from cyclic or acyclic dicarboxylic acids, obtained by dimerization of unsaturated C₆- to C₃₀-carboxylic acids, aliphatic, cycloaliphatic and aromatic C₈- to C₃₀-dicarboxylic acids, C₈- to C₃₀-hydroxycarboxylic acids, and mixtures thereof.

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5. The use of oligomers as defined in any of claims 1 to 4 as a component of pharmaceutical and cosmetic preparations, preferably in cosmetic preparations for the treatment of the skin or of the hair, for the modification of rheological properties of compositions based on compounds of low polarity, and as intermediates for the preparation of water-soluble or water-dispersible polyurethanes.

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6. The use of oligomers as defined in any of claims 1 to 4 as or in coatings and as or in treatment agents for nonabsorbent surfaces, preferably metals, plastics, synthetic textile fibers and glass, and for absorbent surfaces, preferably wood, paper, cotton and leather, and as thickeners for liquids of low polarity.

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7. An oligomer of components A) and B4) and of components A), B1) and C), as defined in any of claims 1 to 4.

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8. A water-soluble or water-dispersible polyurethane of:

Translation of amended sheets annexed to the IPER

64

- a) at least one oligomer, as defined in any of claims 1 to 4,
- b) at least one compound having a molecular weight in the range from 56 to 600, which contains two active hydrogen atoms per molecule,
- 5 c) at least one compound which has two active hydrogen atoms and at least one ionogenic and/or ionic group per molecule,
- d) optionally at least one polymer having at least two active hydrogen atoms per molecule,
- 10 e) at least one diisocyanate.
9. A process for the preparation of a polyurethane, as defined in claim 8, by reacting at least one oligomer a) and the compounds of components b), c) and optionally d) with the diisocyanate component e), where the preparation of the oligomers a) and the preparation of the polyurethane takes place without isolation of an intermediate.
- 15 10. A cosmetic or pharmaceutical composition which comprises at least one polyurethane as claimed in claim 8.
11. A cosmetic composition as claimed in claim 10, in the form of a hair-treatment composition, comprising
- 25 a) 0.5 to 20% by weight of at least one polyurethane, as defined in claim 15,
- b) 50 to 99.5% by weight of at least one solvent, chosen from water, water-miscible solvents and mixtures thereof,
- 30 c) 0 to 70% by weight, preferably 0.1 to 50% by weight, of a propellant,
- d) 0 to 10% by weight of a water-soluble or -dispersible hair polymer which is different from a),
- 35 e) 0 to 0.5% by weight of a water-soluble or water-dispersible silicone compound,
- 40 f) 0 to 1% by weight, preferably 0.0001 to 0.5% by weight, of at least one compound chosen from esters and amides of saturated and mono- or polyunsaturated C₅- to C₃₀-carboxylic acids, saturated and mono- or polyunsaturated C₈- to C₃₀-alcohols and mixtures thereof.
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Translation of amended sheets annexed to the IPER

65

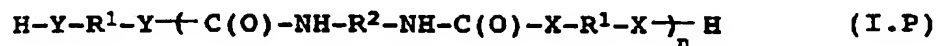
12. The use of the polyurethanes as defined in claim 8 as auxiliaries in cosmetics, preferably as coatings for hair, skin and nails, in particular in hair cosmetics, preferably as setting polymers in hair sprays, setting foams, hair mousse, hair gel and shampoos.
13. The use of the polyurethanes as claimed in claim 8 in decorative cosmetics, preferably in mascara, make-up and eyeshadows, as polymeric emulsifier or co-emulsifier for the formulation of cosmetic or pharmaceutical preparations, and as auxiliaries in pharmacy, preferably as or in coatings or binders for solid medicament forms.
14. The use of the polyurethanes as defined in claim 8 as or in coatings for the textile, paper, printing, leather and adhesives industry, and as polymer emulsifier for non-cosmetic preparations.
15. A cosmetic composition, comprising:
- i) at least one oil-soluble polyurethane which comprises, in incorporated form,
 - A) at least one aliphatic diisocyanate,
 - B) at least one compound having at least two groups which are reactive toward isocyanate groups, which is chosen from
 - B1) aliphatic and cycloaliphatic polyols, polyamines and/or aminoalcohols,
 - B2) polyetherols and/or diaminopolyethers,
 - B3) polysiloxanes having at least two active hydrogen atoms per molecule,
 - B4) polyester polyols,and mixtures thereof, and
 - C) optionally at least one dicarboxylic acid and/or hydroxycarboxylic acid,
- ii) at least one cosmetically compatible hydrophobic compound,
 - iii) optionally at least one cosmetic active substance different from ii) and

Translation of amended sheets annexed to the IPER

66

iv) optionally at least one additive.

16. A composition as claimed in claim 15, where the polyurethane is obtainable by reacting at least one compound of the formula I.P



in which

R^1 is C_2 - to C_{12} -alkylene, C_5 - to C_8 -cycloalkylene or arylene, where alkylene radicals may be interrupted by one or two C_5 - to C_8 -cycloalkylene or arylene radicals,

R^2 is a radical derived from an aliphatic, cycloaliphatic or aromatic diisocyanate after removal of the isocyanate groups,

X in each repeat unit, is O once and A^1 once,

Y is O once and A^1 once,

A^1 is O or NR^3 , where R^3 is hydrogen, C_1 - to C_6 -alkyl or C_5 - to C_8 -cycloalkyl, and

n is an integer from 1 to 20, and preferably 1 to 5,

with at least one carboxylic acid C) which is chosen from cyclic or acyclic dicarboxylic acids, obtained by dimerization of unsaturated C_6 - to C_{30} -carboxylic acids, aliphatic, cycloaliphatic and aromatic C_8 - to C_{30} -dicarboxylic acids, C_8 - to C_{30} -hydroxycarboxylic acids, and mixtures thereof.

17. The use of the oil-soluble polyurethanes as defined in claim 15, as or in cosmetic oil, pomade, ointment and wax bases, for the formulation of O/W and W/O emulsions, as component of pharmaceutical and cosmetic preparations, preferably in cosmetic preparations for the treatment of the skin or of the hair, for modifying the rheological properties of compositions based on compounds of low polarity, as or in coatings and as or in treatment compositions for nonabsorbent surfaces, preferably metals, plastics, synthetic textile fibers and glass, and for absorbent surfaces, preferably wood, paper, cotton and leather, and as thickeners for liquids of low polarity.